Pd/Cu bimetallic catalysis to access highly fluorinated biaryls from aryl halides and fluorinated arenes

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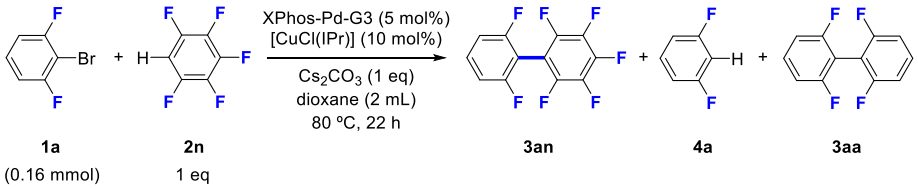
General Experimental Section

All the manipulations were performed in a dry glovebox or by means of standard Schlenk techniques under N_2 or Ar atmosphere. Solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents,[1] and were sparged with nitrogen gas. Solvents for experiments in an inert atmosphere were stored into flame-dried Schlenk flasks over freshly activated 3 or 4 Å molecular sieves. Commercially available chemicals were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem and Acros Organics and were used without further purification. CyPhos-HF and CyPhos-FF, [2] [CuCl(NHC)] complexes,[3] [Cu(C_6F_5)(IPr)][4] and C_6F_5–D,[5] were prepared by reported methods. Flash chromatography was carried out using silica gel (230-240 mesh). Chemical yields refer to pure isolated substances.

NMR spectra were recorded with Bruker Avance 400 Ultrashield and Varian 500/54 Premium Shielded instruments. Chemical shifts are reported in ppm referenced to tetramethylsilane (^{1}H), CCl_3F (^{19}F), and 85% H_3PO_4 (^{31}P), with positive shifts downfield, at 298 K unless otherwise stated. In the ^{19}F and ^{31}P NMR spectra registered in non-deuterated solvents, a coaxial tube containing acetone-d_6 was used to maintain the ^{2}H lock signal.

HRMS (EI) were performed with a MALDI Bruker Autoflex at the LTI facilities of Valladolid University (Spain).

Optimization of Catalytic Conditions



Screening reactions were conducted on a 0.160 mmol scale of aryl halide, in 2.0 mL of solvent (0.08 M). [Pd] precatalyst (0.016 mmol), [Cu] precatalyst (0.032 mmol) and base (0.160 mmol) were added to a flame-dried screwed-capped Schlenk flask with a magnetic stirrer. Then, the corresponding aryl halide (**1a**, 0.160 mmol), arene (**2n**, 0.160 mmol) and solvent (2 mL) were added to the flask. α,α,α-trifluorotoluene was added as internal standard (12.5 µL, 0.100 mmol). The Schlenk was placed in an oil bath at 80 °C and stirred for 22 hours. Then, it was taken out of the bath, cooled to room temperature, and an aliquot was checked by ^{19}F NMR. **3an** was obtained in 74 % yield employing the standard conditions stated in the image.

Table ESI1. Control experiments

When the reaction was carried out in the absence of one or both precatalyst, only traces of coupling product were observed (Table ESI1).

Entry	Conditions	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	Standard	74	4/4
2	No Cu	2	3/3
3	No Pd	<1	-/-
4	No Cu, no Pd	<1	-/-

Standard conditions: **1a** (0.16 mmol), **2n** (0.16 mmol), XPhos-Pd-G3 (5 %), [CuCl(IPr)] (10 %), Cs_2CO_3 (0.16 mmol), dioxane (2 mL), 80 °C, 22 h. [a] Yield determined by ^{19}F NMR.

Table ESI2. Variation of the aryl halide

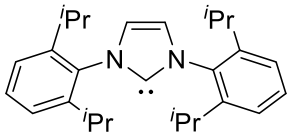
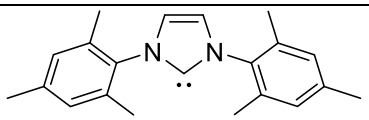
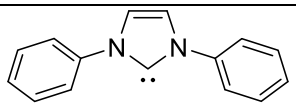
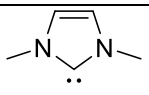
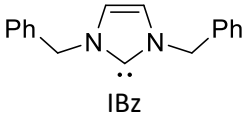
Employing 2-chloro-1,3-difluorobenzene gave the product in a similar yield (entry 2). However, when 1,3-difluoro-2-iodobenzene was used the yield diminished (entry 3).

Entry	Aryl halide	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	Aryl bromide	74	4/4
2	Aryl chloride	70	5/1
3	Aryl iodide	38	4/2

Standard conditions: *Aryl halide* (0.16 mmol), **2n** (0.16 mmol), XPhos-Pd-G3 (5 %), [CuCl(IPr)] (10 %), Cs_2CO_3 (0.16 mmol), dioxane (2 mL), 80 °C, 22 h. [a] Yield determined by ^{19}F NMR.

Table ESI3. Variation of the copper ligand

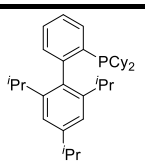
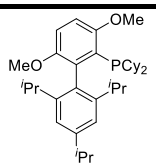
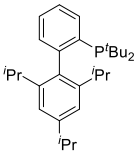
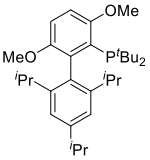
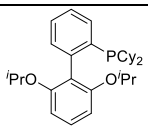
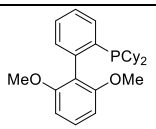
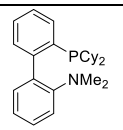
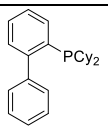
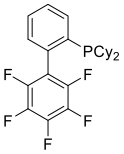
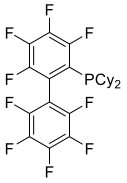
Different [CuCl(NHC)] precatalyst were tested. Only [CuCl(IPr)] gave the product in good yield.

Entry	Ligand	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	 IPr	74	4/4
2	 IMes	9	2/-
3	 IPh	2	-/-
4	 IDm	2	-/-
5	 IBz	1	-/-

Standard conditions: **1a** (0.16 mmol), **2n** (0.16 mmol), XPhos-Pd-G3 (5 %), *[CuCl(L)]* (10 %), Cs_2CO_3 (0.16 mmol), dioxane (2 mL), 80 °C, 22 h. [a] Yield determined by ^{19}F NMR.

Table ESI4. Variation of palladium ligand

Different L-Pd-G3 complexes as well as [Pd(allyl)Cl(IPr)] were tested as precatalyst. The use of bulky ^{t}Bu phosphines (^{t}BuXPhos, ^{t}BuBrettPhos, P^{t}Bu$_3$) was detrimental for the catalysis.

Entry	Ligand	**3an** (%)[a]	**4a**/**3aa** (%)[a]	Entry	Ligand	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	 XPhos	74	4/4	7	 BrettPhos	4	2/1
2	 ^{t}BuXPhos	27	5/-	8	 ^{t}BuBrettPhos	1	3/-
3	 RuPhos	17	5/-	9	 SPhos	12	4/-
4	 DavePhos	5	6/0	10	 JohnPhos	<1	4/-
5	 CyPhos-HF	5	0/1	11	 CyPhos-FF	<1	0/3
6	P^{t}Bu$_3$	10	5/-	12	[Pd(allyl)Cl(IPr)]	<1	0/1

Standard conditions: **1a** (0.16 mmol), **2n** (0.16 mmol), *L-Pd-G3* (5 %), [CuCl(IPr)] (10 %), Cs_2CO_3 (0.16 mmol), dioxane (2 mL), 80 °C, 22 h. [a] Yield determined by ^{19}F NMR.

Table ESI5. Solvent Screening

Different solvents where tested, the use of toluene diminished the reaction yield, while employing a coordinating solvent such as acetonitrile did not afford the coupling product (Table ESI5).

Entry	Conditions	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	1,4-dioxane	74	4/4
2	THF	64	8/-
3	Toluene	18	3/2
4	Acetonitrile	<1	6/-

Standard conditions: **1a** (0.16 mmol), **2n** (0.16 mmol), XPhos-Pd-G3 (5 %), [CuCl(IPr)] (10 %), Cs_2CO_3 (0.16 mmol), *solvent* (2 mL), 80 °C, 22 h. [a] Yield determined by ^{19}F NMR.

Table ESI6. Base Screening

CsOH gave the product in a moderate yield (Table ESI6, entry 2), while the use of other carbonate salts did not afford the product, probably due to their lower solubility (entries 3,4). Employing NaO^{t}Bu yielded 17% of product, moreover, activation of the para C-F bond of the C_6F_5 moiety was also observed (entry 5). K_3PO_4 was not efficient either (entry 6).

Entry	Conditions	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	Cs_2CO_3	74	4/4
2	CsOH	55	4/5
3	K_2CO_3	3	4/2
4	Na_2CO_3	<1	-/-
5	NaO^{t}Bu	17	4/2
6	K_3PO_4	3	3/2

Standard conditions: **1a** (0.16 mmol), **2n** (0.16 mmol), XPhos-Pd-G3 (5 %), [CuCl(IPr)] (10 %), *base* (0.16 mmol), dioxane (2 mL), 80 °C, 22 h. [a] Yield determined by ^{19}F NMR.

Table ESI7. Temperature Screening

Lower yields were obtained when other temperatures were tested (60 – 100 °C) (Table ESI7).

Entry	T (°C)	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	60	53	3/2
2	70	46	2/3
3	80	74	4/4
4	90	52	2/3
5	100	40	4/-

Standard conditions: **1a** (0.16 mmol), **2n** (0.16 mmol), XPhos-Pd-G3 (5 %), [CuCl(IPr)] (10 %), Cs_2CO_3 (0.16 mmol), dioxane (2 mL), *temperature*, 22 h. [a] Yield determined by ^{19}F NMR.

Table ESI8. Concentration Effect

Reducing the amount of copper precatalyst vastly reduced the product yield (Table ESI8, entry 2). Increasing the concentration in the system slightly increased the yield, obtaining the product in 80 % yield (Table ESI8, entry 4). At this concentration, reducing the amount of catalysts to a half led to a much lower yield (Table ESI8, entry 5).

Entry	[Ar-Br] (M)	**3an** (%)[a]	**4a**/**3aa** (%)[a]
1	0.04	46	16/-
2	0.04[b]	6	1/2
3	0.08	74	4/4
4	**0.32**	**80**	**2/3**
5	0.32[c]	20	1/2

Standard conditions: **1a** (0.16 mmol), **2n** (0.16 mmol), XPhos-Pd-G3 (5 %), [CuCl(IPr)] (10 %), Cs_2CO_3 (0.16 mmol), dioxane (*V*), 80 °C, 22 h. [a] Yield determined by ^{19}F NMR. [b] [CuCl(IPr)] (5 %). [c] XPhos-Pd-G3 (2.5 %), [CuCl(IPr)] (5 %).

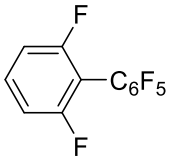
General Procedure for Catalysis

To a flame-dried screwed-capped Schlenk flask with a magnetic stirrer, XPhos-Pd-G3 precatalyst (27.1 mg, 0.032 mmol), [CuCl(IPr)] (31.2 mg, 0.064 mmol) and Cs_2CO_3 (209.0 mg, 0.640 mmol) were added. Then, the corresponding aryl bromide (**1**, 0.640 mmol), fluorinated arene (**2**, 0.640 mmol) and dioxane (2 mL) were added to the flask. The Schlenk was placed in an oil bath at 80 °C and stirred for 22 hours. Then, the flask was taken out of the bath and 5 mL of aqueous saturated NH_4Cl solution were added. The aqueous layer was extracted with Et_2O (3 x 5 mL). The organic fraction was dried over $MgSO_4$ and filtered through a short path of silica gel. The coloured solution was concentrated and the residue was purified by flash column chromatography.

Reported yields are average of two runs.

Catalysis Products Characterization

2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl (3an)



Following general procedure with 2-bromo-1,3-difluorobenzene (**1a**) and pentafluorobenzene (**2n**). The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent (125.5 mg, 70 % yield).

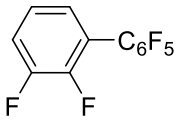
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0116.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.48 (tt, *J* = 8.5, 6.4 Hz, 1H), 7.09 – 7.04 (m, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 160.3 (dd, *J* = 252.5, 5.7 Hz, 2C), 144.6 (d, *J* = 254.9 Hz, 2C), 141.7 (d, *J* = 242.6 Hz, 1C), 137.7 (d, *J* = 255.2 Hz, 2C), 132.1 (t, *J* = 10.2 Hz, 2C), 111.6 (d, *J* = 25.1 Hz, 2C). C_{ipso} not observed.

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -110.17 – -110.31 (m), -137.91 – -138.05 (m), -152.60 (tt, *J* = 20.8, 2.0 Hz), -161.74 – -161.90 (m).

2,2',3,3',4,5,6-heptafluoro-1,1'-biphenyl (3bn)



Following general procedure with 1-bromo-2,3-difluorobenzene (**1b**) and pentafluorobenzene (**2n**). The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent (148.8 mg, 83 % yield).

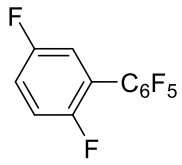
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0127.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 1H), 7.25 – 7.18 (m, 1H), 7.16 – 7.08 (m, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 151.1 (dd, *J* = 249.0, 11.8 Hz, 1C), 148.50 (dd, *J* = 252.3, 13.1 Hz, 1C), 144.5 (dddt, *J* = 250.0, 11.1, 7.4, 3.9 Hz, 2C), 141.6 (dddd, *J* = 255.6, 13.4, 8.3, 5.0 Hz, 1C), 139.6 – 136.2 (dm, *J* = 253.0 Hz, 2C), 126.9 (d, *J* = 3.7 Hz, 1C), 124.6 (dd, *J* = 7.0, 4.8 Hz, 1C), 119.0 (d, *J* = 17.2 Hz, 1C), 116.5 (d, *J* = 12.5 Hz, 1C), 109.2 (tt, *J* = 18.5, 3.5 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -136.21 – -136.53 (m, 1F), -136.85 – -137.16 (m, 1F), -139.98 – -140.15 (m, 2F), -153.10 (tt, J = 20.6, 1.7 Hz, 1F), -161.52 – -161.73 (m, 2F).

2,2',3,4,5,5',6-heptafluoro-1,1'-biphenyl (3cn)



Following general procedure with 2-bromo-1,4-difluorobenzene (**1c**) and pentafluorobenzene (**2n**). The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent (156.0 mg, 87 % yield).

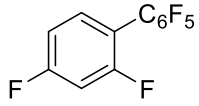
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0129.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.22 – 7.14 (m, 2H), 7.11 – 7.03 (m, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 158.5 (d, *J* = 244.0 Hz, 1C), 156.2 (d, *J* = 247.2 Hz, 1C), 144.4 (d, *J* = 254.2 Hz, 2C), 141.6 (d, *J* = 255.5 Hz, 1C), 137.9 (d, *J* = 252.7 Hz, 2C), 118.6 (d, *J* = 24.9 Hz), 118.5 (dd, *J* = 23.5, 8.8 Hz, 1C), 117.5 (dd, *J* = 24.6, 8.8 Hz, 1C), 115.5 (dd, *J* = 18.0, 9.6 Hz, 1C), 109.3 (s, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -117.98 – -118.17 (m, 1F), -118.55 – -118.72 (m, 1F), -140.06 (dddd, *J* = 22.9, 11.4, 7.2, 3.1 Hz, 2F), -152.98 (t, *J* = 21.1 Hz, 1F), -161.44 – -161.62 (m, 2F).

2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl (3dn)



Following general procedure with 1-bromo-2,4-difluorobenzene (**1d**) and pentafluorobenzene (**2n**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (141.6 mg, 79 % yield).

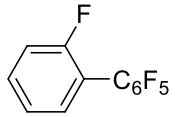
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0119.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 1H), 7.06 – 6.96 (m, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 164.1 (dd, *J* = 252.6, 11.8 Hz, 1C), 160.4 (dd, *J* = 253.4, 12.2 Hz, 1C), 146.1 – 143.3 (m, *J* = 242.7 Hz, 2C), 143.0 – 140.1 (m, *J* = 253.0 Hz, 1C), 139.4 – 135.9 (m, *J* = 247.8 Hz, 2C), 133.0 (dd, *J* = 9.9, 3.8 Hz, 1C), 112.1 (dd, *J* = 21.6, 3.8 Hz, 1C), 110.4 (d, *J* = 16.3 Hz, 1C), 109.5 (td, *J* = 18.5, 4.1 Hz, 1C), 104.9 (t, *J* = 25.5 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -106.69 – -106.80 (m, 1F), -108.13 (h, *J* = 9.7 Hz, 1F), -140.28 – -140.42 (m, 2F), -153.63 (t, *J* = 20.8 Hz, 1F), -161.74 – -161.94 (m, 2F).

2,2',3,4,5,6-hexafluoro-1,1'-biphenyl (3en)



Following general procedure with 1-bromo-2-fluorobenzene (**1n**) and pentafluorobenzene (**2n**). The product was obtained as a colourless liquid after column chromatography employing *n*-pentane as eluent (151.0 mg, 90 % yield).

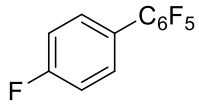
HRMS (EI) Calculated for $C_{12}H_4F_6$ $[M]^+$: 262.0217. Experimental $[M]^+$: 262.0221.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 1H), 7.39 – 7.34 (m, 1H), 7.28 (td, *J* = 7.5, 1.1 Hz, 1H), 7.26 – 7.20 (m, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 160.1 (d, *J* = 250.7 Hz, 1C), 144.5 (dddt, *J* = 248.9, 11.0, 7.3, 3.8 Hz, 2C), 141.3 (dtt, *J* = 254.7, 13.4, 5.1 Hz, 1C), 139.2 – 136.4 (dm, *J* = 251.2 Hz, 2C), 132.1 (t, *J* = 1.9 Hz, 1C), 131.9 (d, *J* = 8.5 Hz, 1C), 124.5 (d, *J* = 3.8 Hz, 1C), 116.2 (s, 1C), 114.4 (dq, *J* = 15.8, 2.0 Hz, 1C), 110.3 (td, *J* = 18.6, 4.0 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -112.73 – -113.12 (m, 1F), -140.29 – -140.52 (m, 2F), -154.29 (t, *J* = 20.7 Hz, 1F), -162.18 – -162.34 (m, 2F).

2,3,4,4',5,6-hexafluoro-1,1'-biphenyl (3fn)



Following general procedure with 1-bromo-4-fluorobenzene (**1f**) and pentafluorobenzene (**2n**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (137.6 mg, 82 % yield).

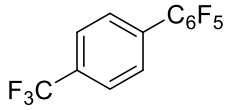
HRMS (EI) Calculated for $C_{12}H_4F_6$ $[M]^+$: 262.0217. Experimental $[M]^+$: 262.0215.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.45 – 7.37 (m, 2H), 7.24 – 7.15 (m, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 163.3 (d, *J* = 249.9 Hz, 1C), 144.3 (dddt, *J* = 247.7, 11.1, 7.5, 3.9 Hz, 2C), 142.0 – 139.4 (m, *J* = 251.9 Hz, 1C), 139.3 – 136.5 (m, *J* = 248.5 Hz, 2C), 132.2 (dd, *J* = 8.5, 2.1 Hz, 2C), 122.4 (s, 1C), 116.1 (d, *J* = 21.9 Hz, 2C), 115.1 (td, *J* = 17.1, 4.1 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -111.33 (tt, *J* = 8.3, 5.4 Hz, 1F), -143.36 (m, 2F), -155.25 (t, *J* = 21.1 Hz, 1F), -161.21 – -163.05 (m, 2F).

2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl (3gn)



Following general procedure with 4-bromobenzotrifluoride (**1g**) and pentafluorobenzene (**2n**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (163.8 mg, 82 % yield).

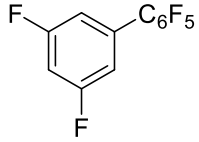
HRMS (EI) Calculated for $C_{13}H_4F_8$ $[M]^+$: 312.0185. Experimental $[M]^+$: 312.0190.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 144.3 (d, *J* = 248.9 Hz, 2C), 141.1 (d, *J* = 255.2 Hz, 1C), 138.1 (d, *J* = 253.1 Hz, 2C), 131.6 (q, *J* = 32.8 Hz, 1C), 130.8 (s, 2C), 130.3 (s, 1C), 126.0 – 125.7 (m, 2C), 123.9 (q, *J* = 271.7 Hz, 1C), 114.7 (td, *J* = 17.0, 4.1 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -62.99 (s, 3F), -142.90 – -143.02 (m, 2F), -153.78 (t, *J* = 21.0 Hz, 1F), -161.32 – -161.50 (m, 2F).

2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl (3hn)



Following general procedure with 1-bromo-3,5-difluorobenzene (**1h**) and pentafluorobenzene (**2n**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (148.8 mg, 83 % yield).

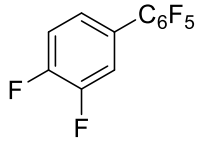
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0126.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.00 – 6.96 (m, 2H), 6.93 (tt, *J* = 8.8, 2.3 Hz, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 163.1 (dd, *J* = 249.8, 12.9 Hz, 2C), 144.2 (d, *J* = 249.7 Hz, 2C), 141.2 (d, *J* = 255.8 Hz, 1C), 138.1 (d, *J* = 251.8 Hz, 2C), 129.3 (d, *J* = 11.3 Hz, 1C), 114.0 (t, *J* = 14.8 Hz, 1C), 113.8 – 112.4 (m, 2C), 105.2 (t, *J* = 25.0 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -101.14 – -112.97 (m, 2F), -138.39 – -145.19 (m, 2F), -153.35 (t, *J* = 21.0 Hz, 1F), -156.20 – -164.29 (m, 2F).

2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl (3in)



Following general procedure with 4-bromo-1,2-difluorobenzene (**1i**) and pentafluorobenzene (**2n**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (141.6 mg, 79 % yield).

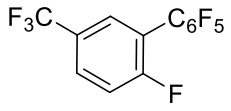
HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0128.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.21 – 7.14 (m, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 151.1 (dd, *J* = 252.0, 12.1 Hz, 1C), 150.5 (dd, *J* = 249.7, 12.7 Hz, 1C), 145.5 – 142.8 (m, *J* =248.6 Hz, 2C), 142.3 – 139.6 (m, *J* =254.3 Hz, 1C), 139.4 – 136.5 (m, *J* = 252.9 Hz, 2C), 126.9 (dq, *J* = 5.9, 2.6 Hz, 1C), 123.1 (s, 1C), 119.7 (d, *J* = 19.0 Hz, 1C), 118.0 (d, *J* = 17.7 Hz, 1C), 114.1 (td, *J* = 17.2, 16.8, 4.5 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -135.55 – -135.69 (m, 1F), -136.26 – -136.40 (m, 1F), -143.00 – -143.11 (m, 2F), -154.10 (t, *J* = 21.0 Hz, 1F), -161.35 – -161.60 (m, 2F).

2,2',3,4,5,6-hexafluoro-5'-(trifluoromethyl)-1,1'-biphenyl (3jn)



Following general procedure with 1-bromo-3-fluoro-5-(trifluoromethyl)benzene (**1j**) and pentafluorobenzene (**2n**). The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent (179.6 mg, 85 % yield).

HRMS (EI) Calculated for $C_{13}H_3F_9$ $[M]^+$: 330.0091. Experimental $[M]^+$: 330.0083.

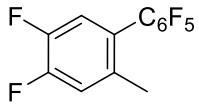
^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 1H), 7.71 – 7.65 (m, 1H), 7.37 (t, *J* = 8.8 Hz, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 257.0 Hz, 1C), 144.6 (dddt, *J* = 250.3, 11.0, 7.7, 3.9 Hz, 2C), 141.9 (dtt, *J* = 256.3, 13.4, 5.1 Hz, 1C), 139.7 – 136.4 (dm, *J* = 251.9 Hz, 2C), 130.1 – 129.7 (m, 1C), 129.3 (dq, *J* = 9.5, 3.7 Hz, 1C), 127.6 (qd, *J* = 33.6,

3.6 Hz, 1C), 123.6 (q, *J* = 272.0 Hz, 1C), 117.2 (d, *J* = 23.0 Hz, 1C), 115.5 (dq, *J* = 17.4, 2.0 Hz, 1C), 108.9 (td, *J* = 18.2, 4.1 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -62.48 (s, 3F), -104.00 – -109.23 (m, 1F), -138.19 – -141.72 (m, 2F), -152.79 (t, *J* = 20.6 Hz, 1F), -158.37 – -165.37 (m, 2F).

2,3,4,4',5,5',6-heptafluoro-2'-methyl-1,1'-biphenyl (3kn)



Following general procedure with 1-bromo-4,5-difluoro-2-methylbenzene (**1k**) and pentafluorobenzene (**2n**). The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent (156.3 mg, 83 % yield).

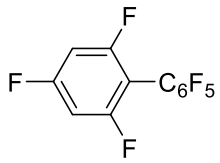
HRMS (EI) Calculated for $C_{13}H_5F_7$ $[M]^+$: 294.0279. Experimental $[M]^+$: 294.0285.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.16 (dd, *J* = 11.1, 7.9 Hz, 1H), 7.04 (dd, *J* = 10.4, 7.9 Hz, 1H), 2.15 (s, 3H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 150.9 (dd, *J* = 251.2, 12.4 Hz, 1C), 148.5 (dd, *J* = 247.8, 13.0 Hz, 1C), 144.3 (dddt, *J* = 247.4, 10.9, 7.2, 3.8 Hz, 2C), 141.3 (dtt, *J* = 254.9, 13.3, 5.1 Hz, 1C), 139.3 – 136.3 (dm, *J* = 251.6 Hz, 2C), 135.0 (dd, *J* = 6.3, 3.9 Hz, 1C), 122.1 (dp, *J* = 6.2, 1.9 Hz, 1C), 119.7 (d, *J* = 18.3 Hz, 1C), 119.3 (d, *J* = 17.4 Hz, 1C), 113.8 (td, *J* = 19.4, 4.1 Hz, 1C), 19.2 (s, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -136.59 (ddd, *J* = 21.5, 11.0, 7.8 Hz, 1F), -140.39 – -140.76 (m, 2F), -141.37 (dt, *J* = 21.5, 9.2 Hz, 1F), -154.29 (t, *J* = 20.7 Hz, 1F), -161.80 – -161.96 (m, 2F).

2,2',3,4,4',5,6,6'-octafluoro-1,1'-biphenyl (3ln)



Following general procedure with 2-bromo-1,3,5-trifluorobenzene (**1l**) and pentafluorobenzene (**2n**). The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent (137.4 mg, 72 % yield).

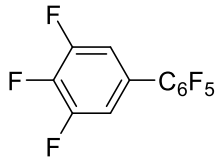
HRMS (EI) Calculated for $C_{12}H_2F_8$ $[M]^+$: 298.0029. Experimental $[M]^+$: 298.0036.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 6.88 – 6.81 (m, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 164.3 (dt, *J* = 253.2, 15.3 Hz, 1C), 160.9 (ddd, *J* = 253.3, 15.2, 9.0 Hz, 2C), 144.8 (dddt, *J* = 250.6, 11.1, 7.3, 3.9 Hz, 2C), 142.1 (dtt, *J* = 256.1, 13.4, 5.2 Hz, 1C), 139.6 – 136.2 (dm, *J* = 251.6 Hz, 2C), 103.6 (td, *J* = 18.8, 4.0 Hz, 1C), 101.5 – 100.7 (m, 2C), 100.6 (d, *J* = 3.2 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -104.08 (p, *J* = 8.2 Hz, 1F), -107.12 (p, *J* = 8.0 Hz, 2F), -138.09 – -138.29 (m, 2F), -152.31 (tt, *J* = 20.8, 2.7 Hz, 1F), -161.68 – -161.88 (m, 2F).

2,3,3',4,4',5,5',6-octafluoro-1,1'-biphenyl (3mn)



Following general procedure with 5-bromo-1,2,3-trifluorobenzene (**1m**) and pentafluorobenzene (**2n**). The product was obtained as a colourless volatile liquid after column chromatography employing *n*-pentane as eluent (135.5 mg, 71 % yield).

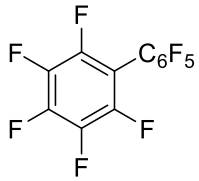
HRMS (EI) Calculated for $C_{12}H_2F_8$ $[M]^+$: 298.0029. Experimental $[M]^+$: 298.0025.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.09 (t, *J* = 6.9 Hz, 1H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 151.5 (ddd, *J* = 251.4, 10.1, 4.2 Hz, 2C), 144.3 (dddt, *J* = 249.7, 10.8, 7.4, 4.0 Hz, 2C), 142.6 – 140.0 (dm, *J* = 256.0 Hz, 1C), 140.6 (dt, *J* = 255.7, 15.2 Hz, 1C), 139.4 – 136.4 (dm, *J* = 252.3 Hz, 2C), 122.4 – 122.0 (m, 1C), 115.0 (ddt, *J* = 17.0, 4.8, 2.2 Hz, 2C), 113.3 (t, *J* = 16.6 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -132.88 – -133.04 (m, 2F), -142.68 – -142.81 (m, 2F), -152.93 (t, *J* = 21.0 Hz, 1F), -157.91 (tt, *J* = 20.7, 6.5 Hz, 1F), -160.80 – -161.00 (m, 2F).

perfluoro-1,1'-biphenyl (3nn)



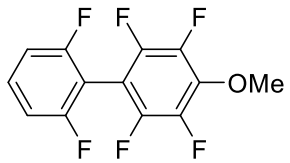
Following general procedure with bromopentafluorobenzene (**1n**) and pentafluorobenzene (**2n**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (136.9 mg, 64 % yield).

HRMS (EI) Calculated for $C_{12}F_{10}$ $[M]^+$: 333.9840. Experimental $[M]^+$: 333.9837.

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 144.8 (ddt, *J* = 253.2, 11.4, 3.4 Hz, 4C), 144.5 – 141.1 (m, *J* = 258.2 Hz, 2C), 139.9 – 136.5 (m, *J* = 252.1 Hz, 4C), 102.1 – 101.1 (m, 2C).

^{19}F NMR (376.21 MHz, Chloroform-*d*) δ -135.34 – -139.60 (m), -149.81 (t, *J* = 21.0 Hz), -160.23 – -160.45 (m).

2,2',3,5,6,6'-hexafluoro-4-methoxy-1,1'-biphenyl (3ap)



Following general procedure with 2-bromo-1,3-difluorobenzene (**1a**) and 1,2,4,5-tetrafluoroanisole (**2p**). The product was obtained as a colourless liquid after column chromatography employing *n*-pentane as eluent (78.5 mg, 42 % yield).

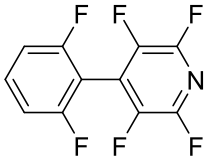
HRMS (EI) Calculated for $C_{13}H_6F_6O$ $[M]^+$: 292.0323. Experimental $[M]^+$: 292.0319.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.44 (tt, *J* = 8.5, 6.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 7.5 Hz, 2H), 4.15 (t, *J* = 1.5 Hz, 3H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 160.5 (dd, *J* = 251.9, 6.3 Hz, 2C), 144.7 (dddd, *J* = 248.7, 12.1, 7.6, 3.9 Hz, 2C), 142.3 – 139.7 (d of m, *J* = 247.0 Hz, 2C), 139.0 (tt, *J* = 11.7, 3.6 Hz, 1C), 131.6 (t, *J* = 10.2 Hz, 1C), 112.2 – 110.9 (m, 2C), 104.7 (tt, *J* = 20.2, 2.2 Hz, 1C), 102.1 (t, *J* = 19.2 Hz, 1C), 62.1 (td, *J* = 3.9, 1.6 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -110.39 (p, *J* = 7.7 Hz, 2F), -140.01 – -140.26 (m, 2F), -158.06 – -158.27 (m, 2F).

4-(2,6-difluorophenyl)-2,3,5,6-tetrafluoropyridine (3aq)



Following general procedure with 2-bromo-1,3-difluorobenzene (**1a**) and 2,3,5,6-tetrafluoropyridine (**2q**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (144.8 mg, 86 % yield).

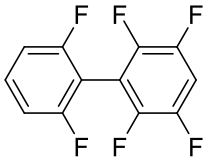
HRMS (EI) Calculated for $C_{11}H_3F_6N$ $[M]^+$: 263.0170. Experimental $[M]^+$: 263.0173.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.56 (tt, *J* = 8.5, 6.5 Hz, 1H), 7.11 (t, *J* = 8.1 Hz, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 159.8 (dd, *J* = 254.2, 6.1 Hz, 2C), 143.5 (dddd, *J* = 246.1, 16.7, 13.1, 3.0 Hz, 2C), 141.4 – 137.4 (d of m, *J* = 262.2 Hz, 2C), 133.3 (t, *J* = 10.2 Hz, 1C), 122.5 (tt, *J* = 17.3, 3.7 Hz, 1C), 112.0 (dd, *J* = 20.8, 4.0 Hz, 2C), 103.5 (t, *J* = 19.9 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -90.18 (tt, *J* = 26.8, 13.4 Hz, 2F), -109.52 (dh, *J* = 17.2, 9.2, 8.8 Hz, 2F), -139.35 (dpd, *J* = 23.2, 14.3, 7.5 Hz, 2F).

2,2',3,5,6,6'-hexafluoro-1,1'-biphenyl (3as)



Following general procedure with 2-bromo-1,3-difluorobenzene (**1a**) and 1,2,4,5-tetrafluorobenzene (**2s**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (100.7 mg, 60 % yield).

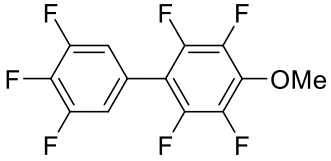
HRMS (EI) Calculated for $C_{12}H_4F_6$ $[M]^+$: 262.0217. Experimental $[M]^+$: 262.0213.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.47 (tt, *J* = 8.4, 6.4 Hz, 1H), 7.18 (tt, *J* = 9.5, 7.4 Hz, 1H), 7.10 – 7.01 (m, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 160.5 (dd, *J* = 252.3, 6.2 Hz, 2C), 147.4 – 144.7 (dm, *J* = 252.2 Hz, 2C), 144.3 (ddt, *J* = 252.1, 16.0, 4.8 Hz, 2C), 132.1 (t, *J* = 10.2 Hz, 1C), 111.8 (dd, *J* = 20.7, 4.5 Hz, 2C), 110.0 (tdd, *J* = 18.3, 3.7, 1.8 Hz, 1C), 107.5 – 106.2 (m, 1C), 105.1 (tt, *J* = 20.3, 2.3 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -110.31 (p, *J* = 7.4 Hz, 2F), -138.72 – -139.12 (m, 4F).

2,3,3',4',5,5',6-heptafluoro-4-methoxy-1,1'-biphenyl (3mp)



Following general procedure with 5-bromo-1,2,3-trifluorobenzene (**1m**) and 1,2,4,5-tetrafluoroanisole (**2p**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (49.6 mg, 25 % yield).

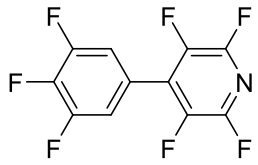
HRMS (EI) Calculated for $C_{13}H_5F_7O$ $[M]^+$: 310.0229. Experimental $[M]^+$: 310.0234.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.22 – 6.89 (m, 2H), 4.14 (t, *J* = 1.5 Hz, 3H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 151.4 (ddd, *J* = 250.8, 10.1, 4.3 Hz, 2C), 145.5 – 143.1 (dm, *J* = 247.7 Hz, 2C), 141.3 (ddt, *J* = 248.2, 15.6, 4.4 Hz, 2C), 140.3 (dt, *J* = 255.0, 14.9 Hz, 1C), 138.9 – 137.0 (m, 1C), 123.2 (tdd, *J* = 8.6, 5.5, 2.5 Hz, 1C), 114.9 (ddt, *J* = 17.2, 5.2, 2.4 Hz, 2C), 111.5 – 110.5 (m, 1C), 62.3 (t, *J* = 4.0 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -133.71 (dd, *J* = 20.7, 8.3 Hz, 2F), -144.93 – -145.03 (m, 2F), -157.36 – -157.50 (m, 2F), -159.05 (tt, *J* = 20.5, 6.6 Hz, 1F).

2,3,5,6-tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine (3mq)



Following general procedure with 5-bromo-1,2,3-trifluorobenzene (**1m**) and 1,2,4,5-tetrafluoropyridine (**2q**). The product was obtained as a colourless liquid after column chromatography employing *n*-pentane as eluent (95.4 mg, 53 % yield).

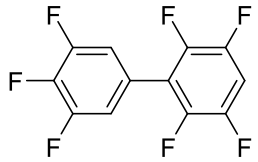
HRMS (EI) Calculated for $C_{11}H_2F_7N$ $[M]^+$: 281.0075. Experimental $[M]^+$: 281.0078.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.26 – 7.21 (m, 2H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 151.5 (ddd, *J* = 252.5, 10.2, 4.1 Hz, 2C), 145.5 – 142.7 (m, 2C), 141.1 (dt, *J* = 258.3, 15.0 Hz, 1C), 140.3 – 137.6 (m, 2C), 130.7 – 129.7 (m, 1C), 121.7 – 121.1 (m, 1C), 115.0 – 114.4 (m, 2C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -89.19 – -89.46 (m, 2F), -132.08 (dd, *J* = 20.7, 7.5 Hz, 2F), -144.54 – -144.72 (m, 2F), -155.61 (tt, *J* = 20.5, 6.7 Hz, 1F).

2,3,3',4',5,5',6-heptafluoro-1,1'-biphenyl (3ms)



Following general procedure with 5-bromo-1,2,3-trifluorobenzene (**1m**) and 1,2,4,5-tetrafluorobenzene (**2s**). The product was obtained as a colourless solid after column chromatography employing *n*-pentane as eluent (104.0 mg, 58 % yield).

HRMS (EI) Calculated for $C_{12}H_3F_7$ $[M]^+$: 280.0123. Experimental $[M]^+$: 280.0117.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.19 – 7.07 (m, 3H).

^{13}C{^{1}H} NMR (125.67 MHz, Chloroform-*d*) δ 151.4 (ddd, *J* = 250.9, 10.1, 4.1 Hz, 2C), 146.5 (dddd, *J* = 249.3, 14.7, 10.4, 4.2 Hz, 2C), 143.8 (ddt, *J* = 248.7, 14.5, 4.1 Hz, 2C), 140.5 (dt, *J* = 255.4, 15.0 Hz, 1C), 123.2 (tdt, *J* = 8.3, 5.2, 2.6 Hz, 1C), 118.7 (t, *J* = 16.2 Hz, 1C), 115.6 – 114.03 (m, 2C), 106.3 (t, *J* = 22.6 Hz, 1C).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -133.49 (dd, *J* = 20.4, 7.9 Hz, 2F), -137.99 – -138.17 (m, 2F), -143.59 (ddd, *J* = 21.0, 12.9, 7.2 Hz, 2F), -158.43 (td, *J* = 14.1, 7.0 Hz, 1F).

X-ray structure of 3bn, 3fn and 3gn

X-ray quality crystals of compounds **3bn**, **3fn** and **3gn** were obtained by slow evaporation of an *n*-pentane solution of the corresponding biaryls. Their X-ray structures are shown in Figure ESI1, Figure ESI2 and Figure ESI3, respectively.

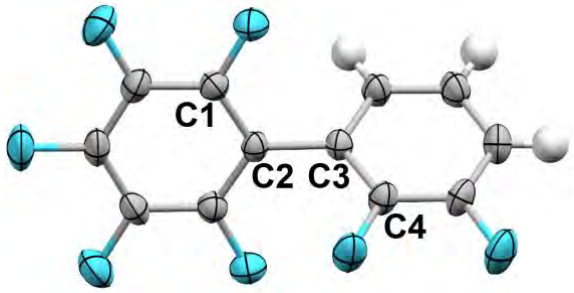


Figure ESI1. X-ray structure of **3bn**. Selected bond distances (Å) and angles (°): C2-C3 = 1.484, C1-C2-C3-C4 = 120.70.

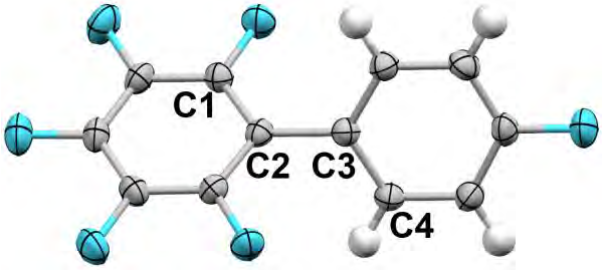


Figure ESI2. X-ray structure of **3fn**. Selected bond distances (Å) and angles (°): C2-C3 = 1.487, C1-C2-C3-C4 = 123.02.

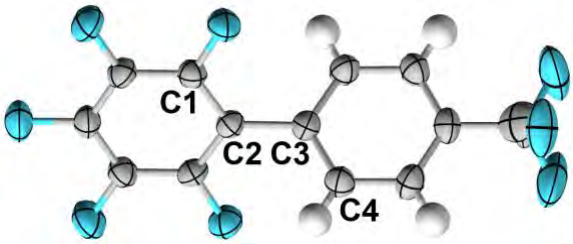
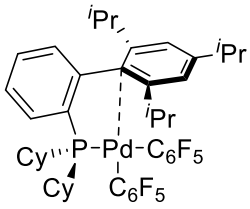


Figure ESI3. X-ray structure of **3gn**. Selected bond distances (Å) and angles (°): C2-C3 = 1.489, C1-C2-C3-C4 = 122.70.

Synthesis of Palladium Intermediates

cis-[Pd(C_6F_5)$_2$(XPhos)] (7) and its X-ray structure



In a flame-dried Schlenk, *cis*-[Pd(C_6F_5)$_2$(THF)$_2$] (97.5 mg, 0.167 mmol) and XPhos (86.2, 0.177 mmol) were dissolved in 3 mL of CH_2Cl_2 at room temperature. The solution was stirred for 1 hour, *n*-hexane (3 mL) was added to induce precipitation of the product and the solvent was removed under vacuum. The colourless solid obtained was sonicated with *n*-pentane, filtered under air and

washed with *n*-pentane (2 x 5 mL). It was dried under vacuum affording the title compound as a colourless solid (130.7 mg, 86 % yield).

X-ray-quality crystals were grown by slow diffusion of a CH_2Cl_2/*n*-hexane mixture at –20 °C.

The X-ray structure of **7** (Figure ESI4) shows a P,C-chelating coordination of XPhos involving predominantly C1 of the distal ring (the Kochi hapticity of this interaction is h = 1.37).[6] The most remarkable structural aspect of **7** is the small C2-Pd-C3 angle (82.3°) forced by the crowding with the biaryl phosphine. This forced angle shortens the distance between C2 and C3 to 2.69 Å, reducing the activation energy for aryl-aryl reductive elimination. Another $[Pd(C_6F_5)_2(PPh_2(biaryl))]$ structure was previously reported.[7]

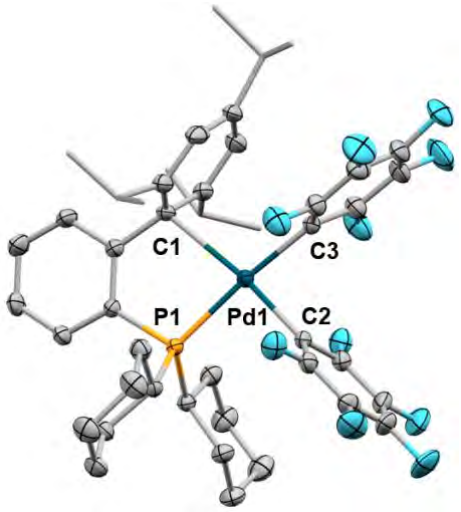


Figure ESI4. X-ray structure of *cis*-$[Pd(C_6F_5)_2(XPhos)]$ (**7**). H atoms omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–P1 = 2.328, Pd1–C1 = 2.478, Pd1–C2 = 2.013, Pd1–C3 = 2.080. P1–Pd1–C1 = 81.58, P1–Pd1–C2 = 91.72, C2–Pd1–C3 = 82.32, C1–Pd1–C3 = 104.32. Pd1–C distances to the two distal ring atoms *ortho* to C1 = 2.784, 3.002.

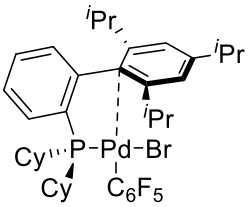
HRMS (EI) Calculated for $C_{45}H_{49}F_{10}NaPPd$ $[M+Na]^+$: 939.2356. Experimental $[M+Na]^+$: 939.2381.

^{1}H NMR (499.72 MHz, Chloroform-*d*) δ 7.68 – 7.62 (m, 1H), 7.50 – 7.41 (m, 2H), 7.06 (s, 2H), 6.89 – 6.85 (m, 1H), 2.47 (hept, J = 6.7 Hz, 2H), 2.15 – 2.00 (m, 5H), 1.86 – 1.78 (m, 2H), 1.77 – 1.64 (m, 14H), 1.31 – 1.17 (m, 6H), 0.99 (d, J = 6.9 Hz, 6H), 0.87 (d, J = 6.6 Hz, 6H), 0.80 – 0.68 (m, 2H).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -111.10 – -111.46 (m, 2F), -112.88 (t, J = 27.4 Hz, 2F), -160.41 (t, J = 20.2 Hz, 1F), -162.44 (t, J = 20.2 Hz, 1F), -163.07 – -163.31 (m, 2F), -163.61 – -163.82 (m, 2F).

^{13}P{^{1}H} NMR (202.30 MHz, Chloroform-*d*) δ 27.8 (s).

[PdBr(C_6F_5)(XPhos)] (8)

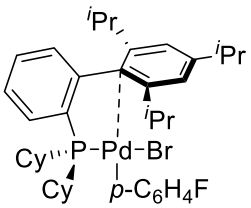


In a flame-dried Schlenk, *cis*-[Pd($CH_2TMS)_2$(COD)] (97.5 mg, 0.167 mmol), XPhos (86.2 mg, 0.177 mmol) and C_6F_5Br (**1n**, 42 µL, 0.33 mmol) were dissolved in 3 mL of THF. The solution was stirred for 3 hours at room temperature, *n*-hexane (3 mL) was added and the mixture was removed under vacuum. The yellowish residue obtained was sonicated with *n*-hexane (*it may be fully redissolved*) and a precipitate appears upon stirring (*overnight stirring is recommended*). It was filtered under air and washed with *n*-pentane (3 x 5 mL). The solid obtained was dried under vacuum affording the title compound as a yellowish solid (80.7 mg, 57 % yield).

In solution this solid shows an equilibria between several species, as observed by low temperature NMR (*vide infra, fluxionality of [PdBr(C_6F_5)(XPhos)]*) which precluded a detailed characterization.

HRMS (EI) Calculated for $C_{39}H_{49}F_5PPd$ $[M-Br]^+$: 749.2536. Experimental $[M-Br]^+$: 749.2556.

[PdBr(*p*-C_6H_4F)(XPhos)] (9)



This complex was prepared following the procedure described to obtain **8** employing 1-bromo-4-fluorobencene (**1f**, 30 µL, 0.27 mmol). The title compound was obtained as a colourless solid (69.2 mg, 67 % yield). The complex is observed as a *cis*/*trans* isomer mixture in solution. (*Major isomer* 88%, *minor isomer* 12%, based on ^{19}F and ^{31}P NMR)

HRMS (EI) Calculated for $C_{39}H_{53}FPPd$ $[M-Br]^+$: 677.2913. Experimental $[M-Br]^+$: 677.2935.

^{1}H NMR (499.72 MHz, Chloroform-*d, only for major isomer*) δ 7.66 (td, J = 6.2, 3.2 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.13 (s, 2H), 6.99 – 6.93 (m, 2H), 6.87 (dt, J = 6.1, 3.3 Hz, 1H), 6.77 – 6.68 (m, 2H), 3.12 (hept, J = 6.8 Hz, 1H), 2.44 (hept, J = 6.8 Hz, 2H), 2.20 (dtd, J = 12.6, 10.0, 3.0 Hz, 2H), 1.96 (bs, 2H), 1.80 (d, J = 12.4 Hz, 2H), 1.75 – 1.65 (m, 6H), 1.59 (d, J = 6.8 Hz, 8H), 1.39 (d, J = 6.9 Hz, 6H), 1.24 – 1.08 (m, 6H), 0.89 (d, J = 6.7 Hz, 6H), 0.74 – 0.56 (m, 2H).

^{19}F NMR (470.17 MHz, Chloroform-*d*) δ -122.64 – -122.75 (m, *minor isomer*), -122.78 – -122.90 (m, *major isomer*).

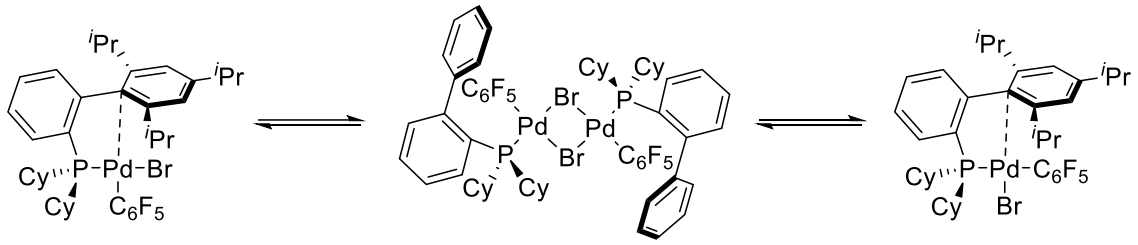
^{13}P{^{1}H} NMR (202.30 MHz, Chloroform-*d*) δ 28.5 (d, J = 2.6 Hz, *minor isomer*), 26.5 (d, J = 3.0 Hz, *major isomer*).

Fluxionality of [PdBr(C_6F_5)(XPhos)] (8)

A solution of **8** in $CDCl_3$ was analysed by ^{19}F and ^{31}P NMR at room temperature (Figure ESI5). When a closer look to the ortho fluorine region of the C_6F_5 moiety is taken in the ^{19}F spectra, it is possible to distinguish a broad signal (-112.1 ppm) and two doublets (-114.8 and -115.8 ppm) in an integer ratio of 45:4:1 (Figure ESI6, top). This behaviour is also

observed for the para and meta fluorine atoms of the C_6F_5 moiety, although signal overlapping precludes a clean analysis of this region of the spectra. To obtain more information, ^{19}F and ^{31}P NMR spectra acquisition was performed at 233 K (Figure ESI7). At this temperature, the broad signal observed in the ortho region of the ^{19}F NMR at room temperature is resolved in at least 5 sharp signals (mainly doublets and triplets), along with the doublets previously observed at room temperature (Figure ESI6, bottom).

Based on the analysis of the NMR spectra, an equilibrium between different species is proposed (Scheme ESI1). The sharp doublets can be assigned to the cis and trans monomers of (**8**). The broad signal observed at room temperature is due to signal coalescence of species in equilibrium, which can be proposed as *μ-Br* Pd dimers. These dimeric species have two intrinsic isomers, *syn* and *anti*, along with conformational isomers due to the unrestricted rotation of the biaryl moiety of the ligand in solution. This kind of ligand fluxionality in halogen-bridged Pd dimers with Buchwald-type phosphine ligands has been previously reported.[8] Moreover, aryl exchange between the Pd species does not take place as no signals of *cis*-[Pd(C_6F_5)$_2$(XPhos)] (**7**) are observed in the spectra.



Scheme ESI1. Dynamic equilibria of **8** in solution. For clarity, only one dimeric species is shown and ^{i}Pr substituents have been omitted in it.

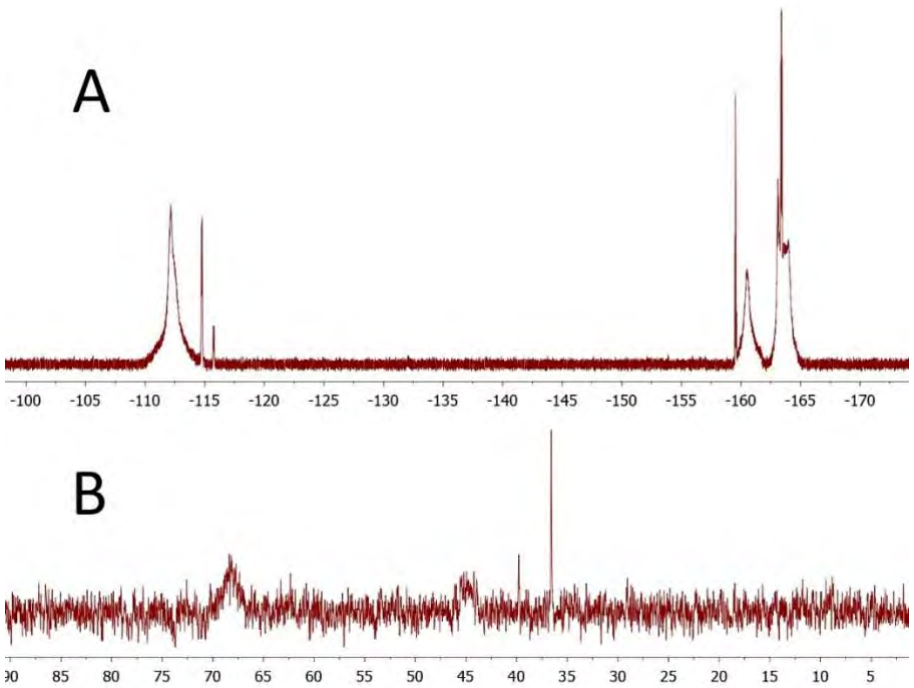


Figure ESI5. ^{19}F (top, A) and ^{31}P (bottom, B) NMR spectra of **8** at 298 K in $CDCl_3$.

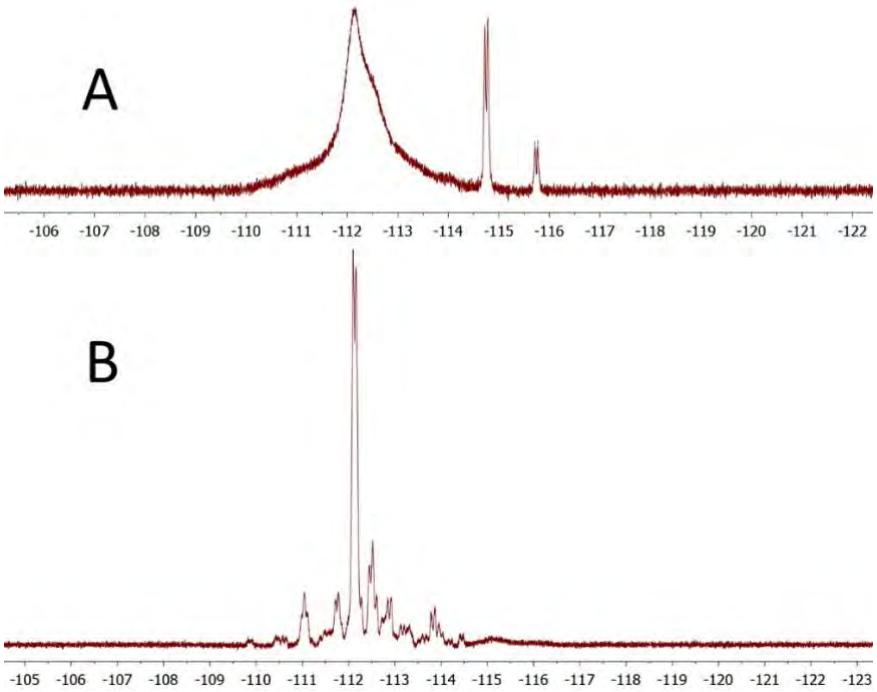


Figure ESI6. Ortho fluorine spectra region of **8** at 298 K (top, A) and 233 K (bottom, B).

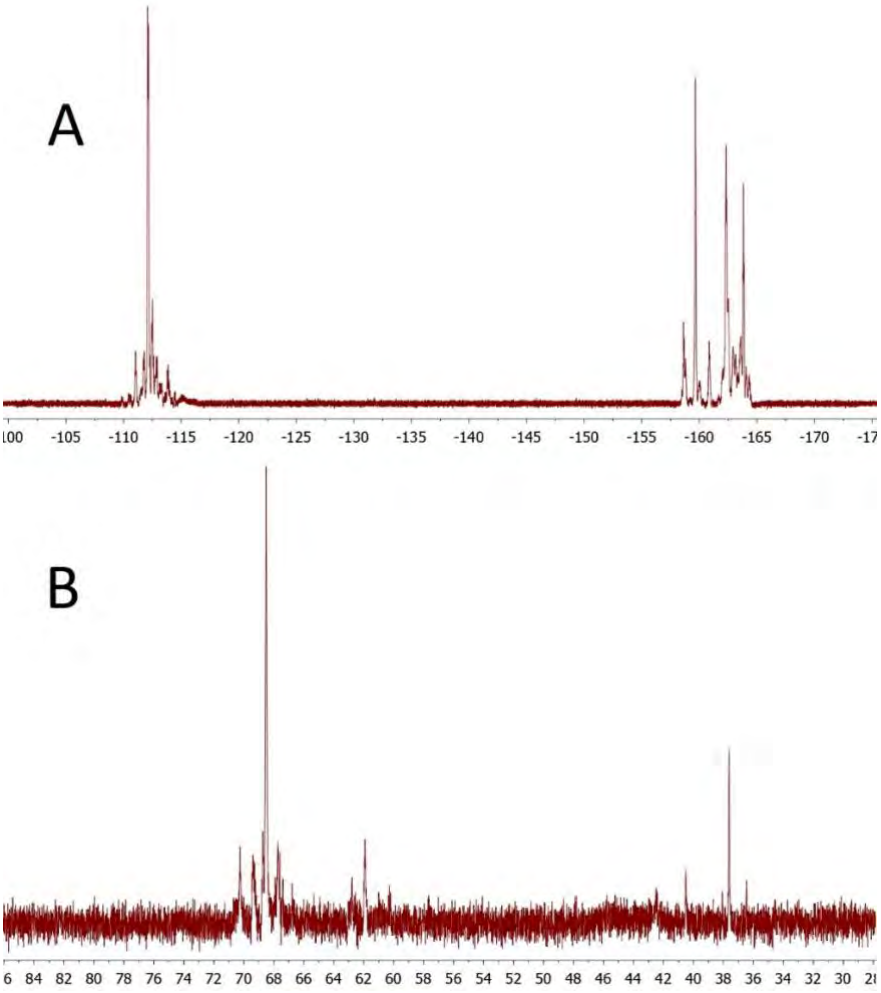


Figure ESI7. ^{19}F (top, A) and ^{31}P (bottom, B) NMR spectra of **8** at 233 K in $CDCl_3$.

Stoichiometric Studies

C-H activation

In a flame-dried Schlenk under N_2 atmosphere, [CuCl(IPr)] (15.8 mg, 32.4 µmol), Cs_2CO_3 (10.6 mg, 32.4 µmol) and C_6F_5H (5.0 µL, 45.0 µmol) were dissolved in 1 mL of dioxane. The solution was stirred at 40 °C. After 2 hours, an aliquot of the mixture was analysed by ^{19}F NMR, showing full conversion to the C–H activation product, [Cu(C_6F_5)(IPr)] (**5**) (Figure ESI8).[9]

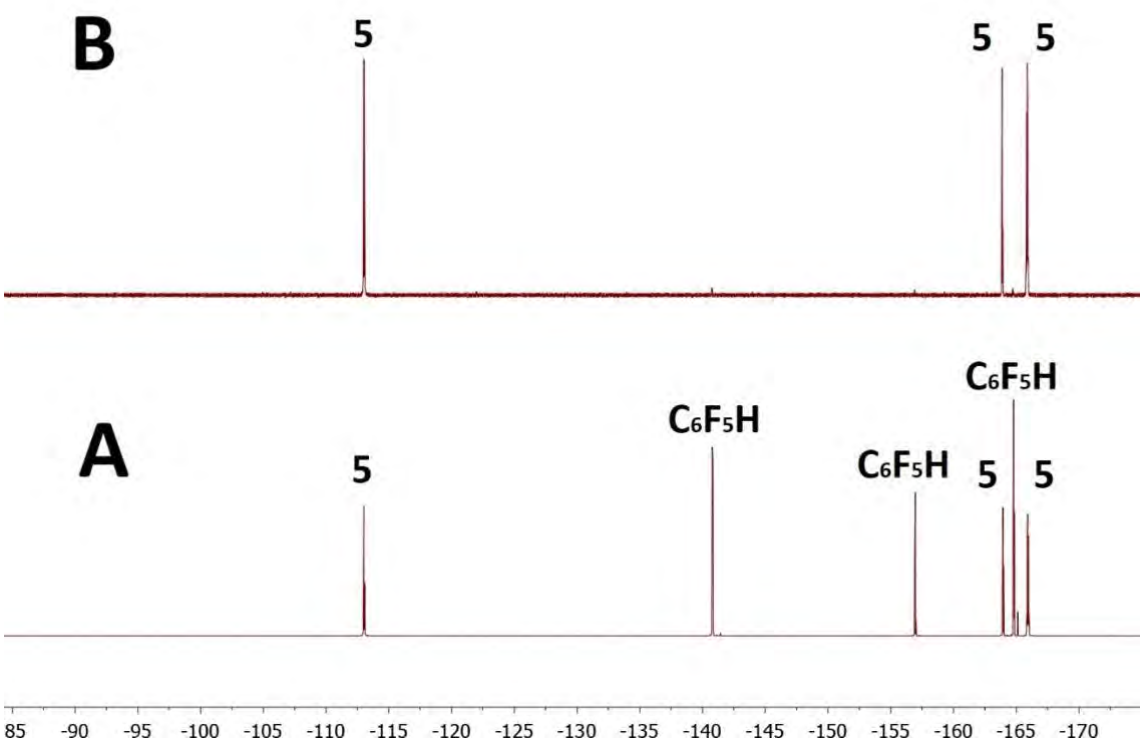


Figure ESI8. ^{19}F NMR spectra after 1 hour (A, bottom) and 2 hours (B, top) of the C–H activation experiment.

Reductive elimination from *cis*-[Pd(C_6F_5)$_2$(XPhos)] (7) and oxidative addition to [PdBr(C_6F_5)(XPhos)] (8)

In a flame-dried Schlenk under N_2 atmosphere, **7** (7.10 mg, 7.75 µmol) and C_6BrF_5 (**1n**, 3.0 µL, 23.2 µmol, 3 eq) were dissolved in 500 µL of dioxane. The mixture was stirred in an oil bath at 80 °C. The reaction was followed by ^{19}F and ^{31}P NMR. After 180 min, signals of **7** had fully disappeared and only signals of **8** were observed in the ^{19}F NMR spectra (Figure ESI9).

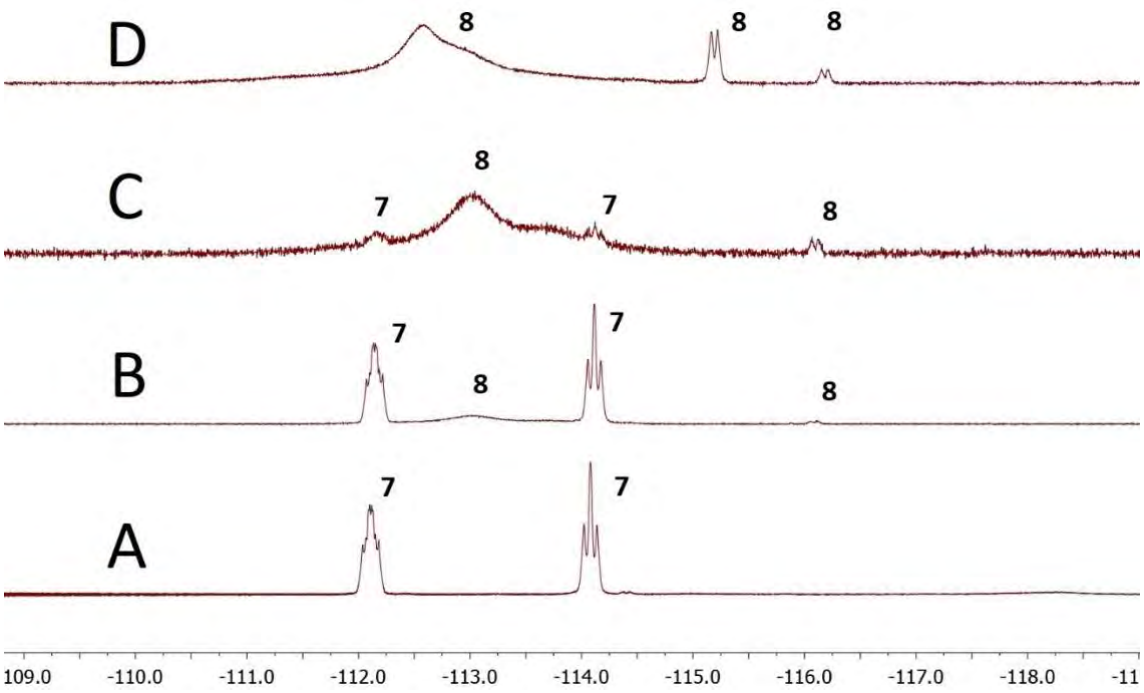


Figure ESI9. Ortho fluorine region of the ^{19}F NMR spectra at 298 K. A (bottom): mixture of *cis*-[Pd(C_6F_5)$_2$(XPhos)] (**7**) and C_6F_5Br (**1n**) at room temperature; B (middle) mixture after 60 min at 80 °C; C (middle) mixture after 120 min at 80 °C; D (top) mixture after 180 min at 80 °C.

Cu to Pd aryl transmetalation

In a flame-dried NMR tube under N_2 atmosphere, [Cu(C_6F_5)(IPr)] (**5**) (5.00 mg, 8.1 µmol) and the corresponding oxidative addition Pd complex, **8** or **9** (1 eq, 8.1 µmol), were dissolved in 500 µL of dioxane at room temperature. The tube was vigorously shaken and ^{19}F and ^{31}P NMR spectra were acquired.

When complex **8** was employed, disappearance of its broad signals and formation of the signals corresponding to *cis*-[Pd(C_6F_5)$_2$(XPhos)] (**7**) was observed (Figure ESI10). In contrast, for **9** not only transmetalation but also reductive elimination took place. Hence, formation of the coupling product *p*-C_6H_4F–C_6F_5 (**3fn**) was observed. This transformation finished in less than 2 hours at room temperature, when no remaining **5** was observed (Figure ESI11, top).

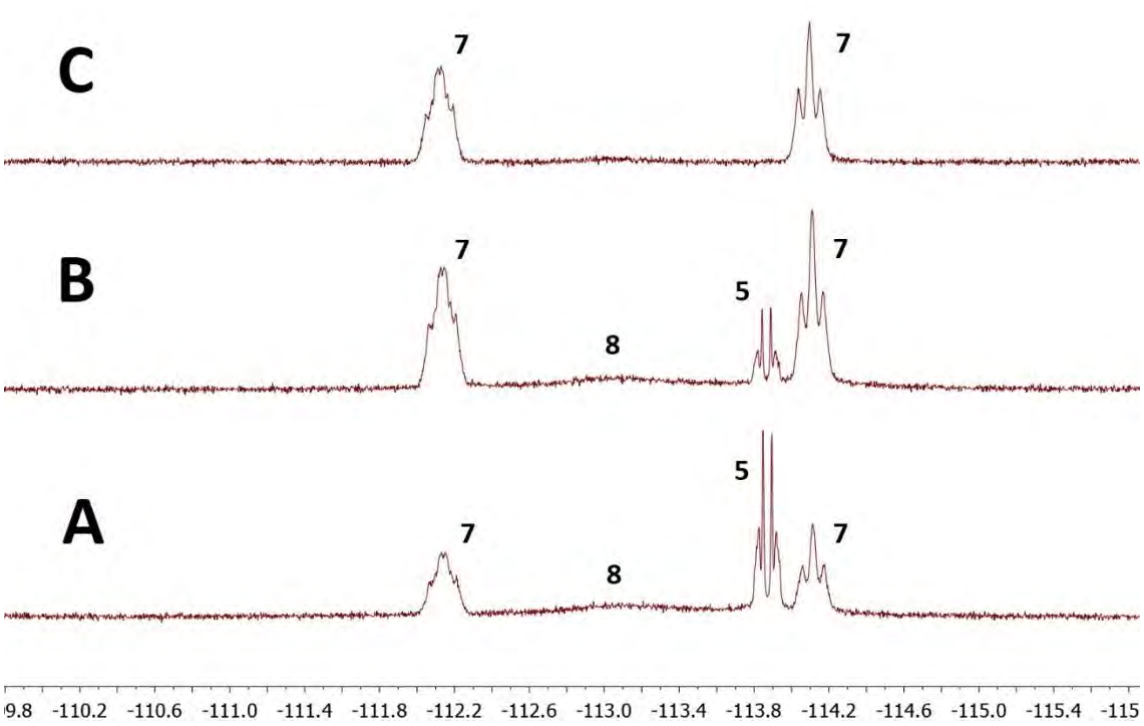


Figure ESI10. ^{19}F NMR spectra of the reaction between **8** and **5** in dioxane at 298 K. A (bottom): acquisition after tube preparation. B (middle): acquisition after 2 hours at 298 K. C (top) acquisition after 4 hours at 298 K.

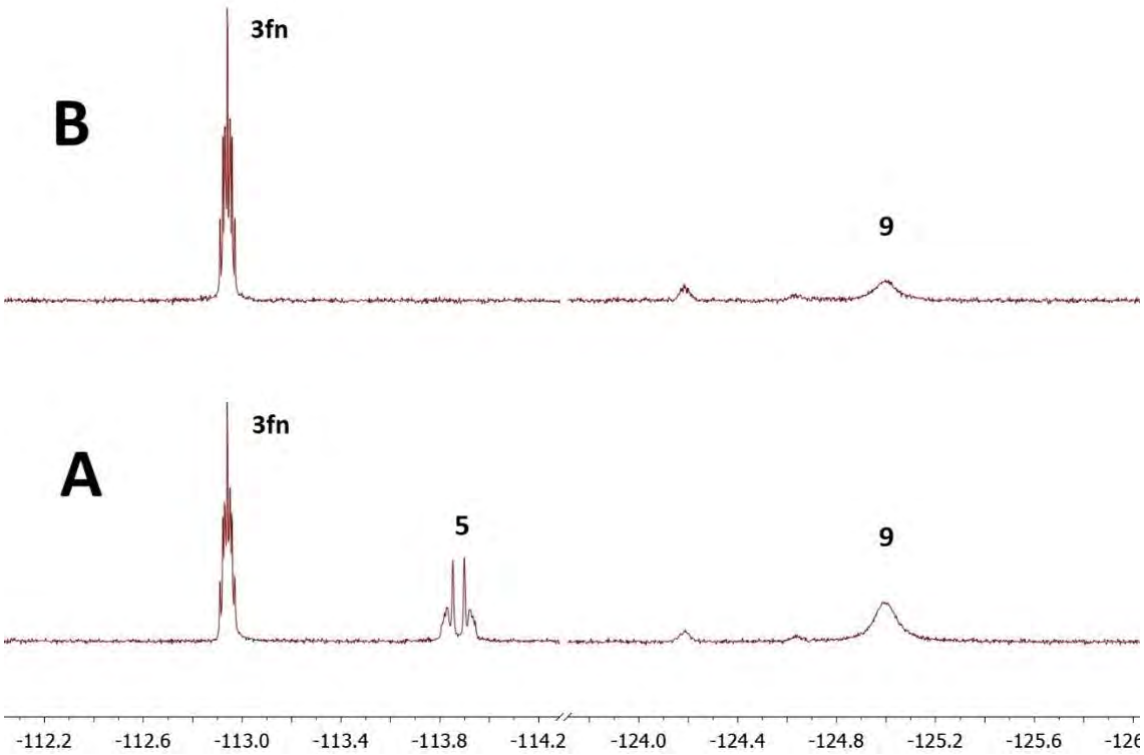


Figure ESI11. ^{19}F NMR spectra of the reaction between **9** and **5** in dioxane at room temperature. A (bottom): acquisition after tube preparation. B (top): acquisition after 2 hours at 298 K.

Detection of reaction intermediates

Following the general procedure for catalysis, when an aliquot of the reaction employing C_6BrF_5 (**1n**) and C_6F_5H (**2n**) was analysed by NMR before hydrolysis, signals of complexes **5** and **7** were detected in the ^{19}F NMR spectra (Figure ESI12). This observation suggests that the reductive elimination is the rate determining step in this reaction.

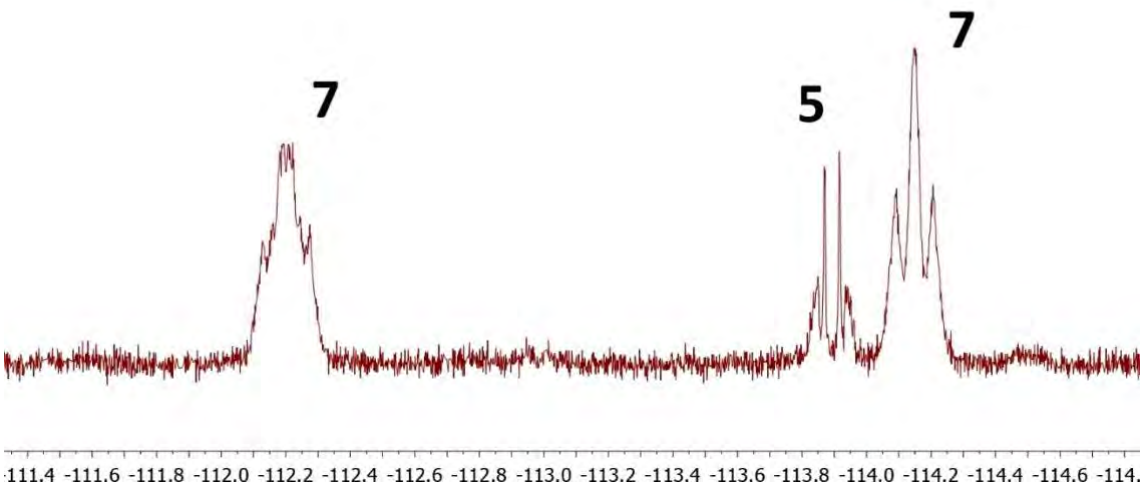


Figure ESI12. Ortho region of the ^{19}F NMR spectra of an aliquot of the catalysis employing **1n** and **2n** as substrates before hydrolysis.

KIE Experiments

KIE experiments were performed by measuring the ratio of product formation between the activation of deuterated and protic reagents in experiments carried out in separated vessels (Figure ESI13, Table ESI9). KIE experiments were conducted following the general procedure for catalysis. α,α,α-trifluorotoluene was added as internal standard. C_6F_5–D was employed instead of C_6F_5–H in the deuterium labelled experiments.

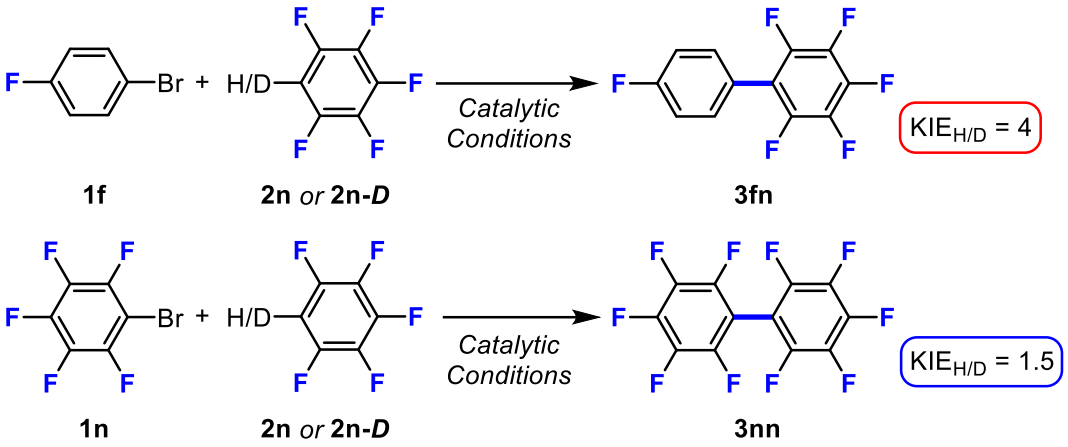


Figure ESI13. KIE experiments employing two different aryl bromides (**1f**, **1n**).

Table ESI9. Product formation in the KIE experiments.

Aryl Bromide	Arene	Time (h)	[Product] (M)	Product Yield (%)	$KIE_{H/D}$
1f	**2n**	1	0.032	10.1	4.0
1f	**2n-*D***	1	0.008	2.5	
1f	**2n**	3	0.168	52.4	4.0
1f	**2n-*D***	3	0.042	13.2	
1n	**2n**	3	0.036	11.2	1.5
1n	**2n-*D***	3	0.023	7.4	

X-ray Crystallographic Data

A crystal was attached to a glass fiber and transferred either to an Agilent Supernova diffractometer with an Atlas CCD area detector (Valladolid University facilities). The crystal was kept at constant temperature during data collection. Data collection was performed with Mo-Kα radiation (λ = 0.71073 Å). Data integration, scaling and empirical absorption correction were carried out using the CrysAlisPro program package.[10] Using Olex2,[11] the structure was solved with the olex2.solve[12] structure solution program and refined with ShelX program.[13] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. Refinement proceeded smoothly to give the residuals shown in Table ESI10 and Table ESI11. CCDC contains the supporting crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table ESI10. Crystal data and structure refinements for compounds **3bn**, **3fn** and **3gn**.

Identification code	**3bn**	**3fn**	**3gn**
CCDC deposition N°	2131398	2131399	2131400
Empirical formula	$C_{12}H_3F_7$	$C_{12}H_4F_6$	$C_{13}H_4F_8$
Formula weight	280.14	262.15	312.16
Temperature/K	294	294	294
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$
a/Å	7.3590(9)	13.3244(14)	14.5626(17)
b/Å	7.5748(9)	5.9453(5)	5.8525(7)
c/Å	9.8836(10)	13.0908(15)	14.0383(11)
α/°	75.019(9)	90	90
β/°	79.707(9)	108.653(13)	93.599(10)
γ/°	78.279(10)	90	90
Volume/Å^3	516.46(11)	982.55(19)	1194.1(2)
Z	2	4	4
ρ_{calc}g/cm^3	1.801	1.772	1.736
μ/mm^{-1}	0.194	0.183	0.189
F(000)	276	520	616
Crystal size/mm^3	0.539 × 0.491 × 0.082	0.744 × 0.479 × 0.189	0.423 × 0.329 × 0.102
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.674 to 58.896	7.576 to 58.966	6.614 to 59.4
Index ranges	-9 ≤ h ≤ 9, -7 ≤ k ≤ 9, -12 ≤ l ≤ 13	-18 ≤ h ≤ 14, -7 ≤ k ≤ 5, -12 ≤ l ≤ 17	-19 ≤ h ≤ 16, -8 ≤ k ≤ 4, -14 ≤ l ≤ 19
Reflections collected	4325	4255	5001
Independent reflections	2392 [R_{int} = 0.0258, R_{sigma} = 0.0517]	2292 [R_{int} = 0.0346, R_{sigma} = 0.0526]	2778 [R_{int} = 0.0289, R_{sigma} = 0.0508]
Data/restraints/parameters	2392/0/172	2292/0/163	2778/0/227
Goodness-of-fit on F^2	1.066	0.963	1.03
Final R indexes [I>=2σ (I)]	R_1 = 0.0504, wR_2 = 0.1023	R_1 = 0.0581, wR_2 = 0.1328	R_1 = 0.0532, wR_2 = 0.1182
Final R indexes [all data]	R_1 = 0.1160, wR_2 = 0.1472	R_1 = 0.1060, wR_2 = 0.1862	R_1 = 0.1408, wR_2 = 0.1764
Largest diff. peak/hole / e Å^{-3}	0.16/-0.23	0.35/-0.37	0.16/-0.21

Table ESI11. Crystal data and structure refinements for compound **7**.

Identification code	$[Pd(C_6F_5)_2(XPhos)]$ (**7**)
CCDC deposition N°	2131401
Empirical formula	$C_{45}H_{49}F_{10}PPd$
Formula weight	917.16
Temperature/K	294
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.2800(5)
b/Å	11.8689(3)
c/Å	17.7116(4)
α/°	90
β/°	104.392(2)
γ/°	90
Volume/Å^3	4129.42(18)
Z	4
ρ_{calc}g/cm^3	1.475
μ/mm^{-1}	0.565
F(000)	1880
Crystal size/mm^3	0.286 × 0.177 × 0.145
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.826 to 59.26
Index ranges	-25 ≤ h ≤ 27, -16 ≤ k ≤ 15, -15 ≤ l ≤ 23
Reflections collected	17887
Independent reflections	9636 [R_{int} = 0.0289, R_{sigma} = 0.0553]
Data/restraints/parameters	9636/1/542
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.0775
Final R indexes [all data]	R_1 = 0.0837, wR_2 = 0.0987
Largest diff. peak/hole / e Å^{-3}	0.44/-0.48

NMR Spectra

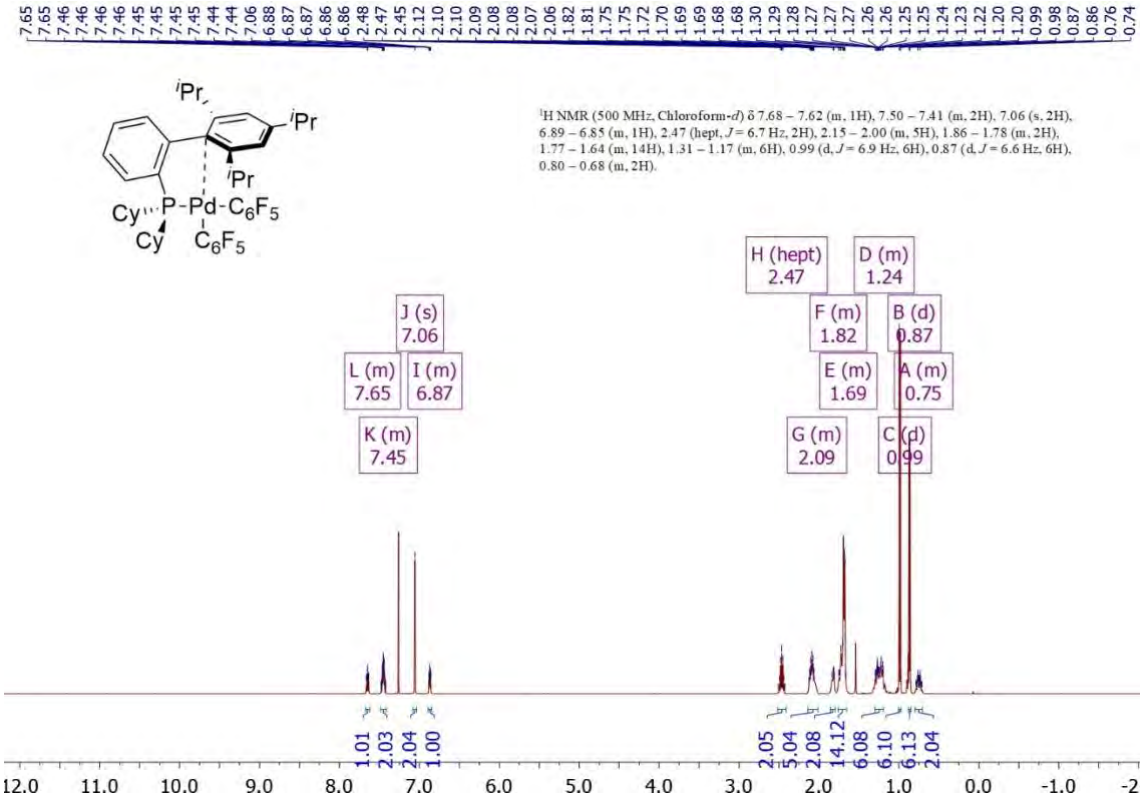


Figure ESI14. ^{1}H NMR of *cis*-[Pd(C_6F_5)$_2$(XPhos)] (**7**) in $CDCl_3$.

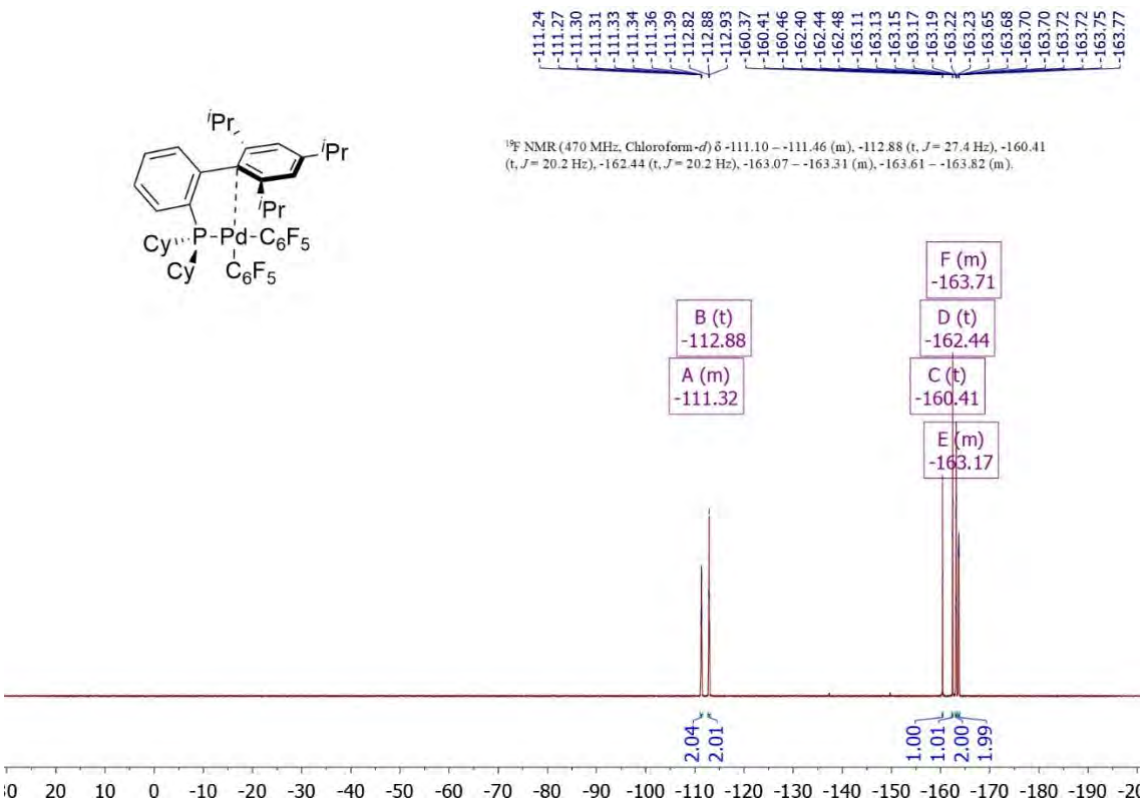


Figure ESI15. ^{19}F NMR of *cis*-[Pd(C_6F_5)$_2$(XPhos)] (**7**) in $CDCl_3$.

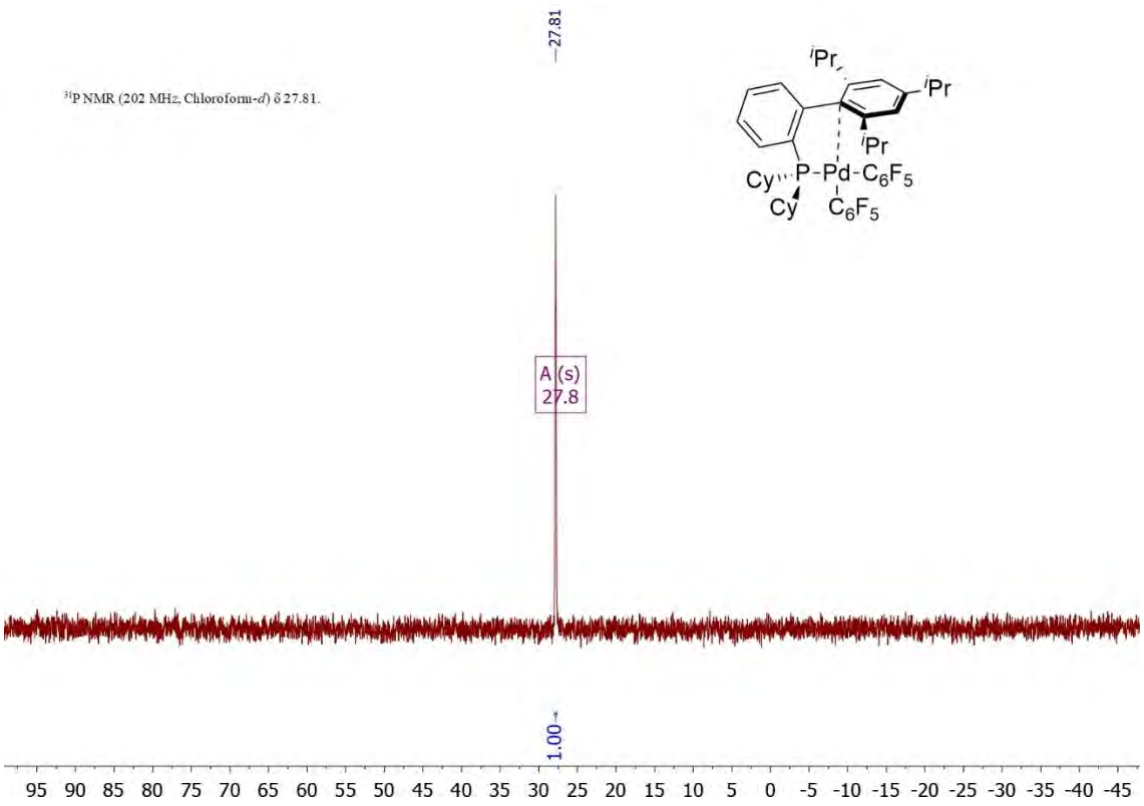


Figure ESI16. $^{31}P\{^{1}H\}$ NMR of *cis*-[Pd(C_6F_5)$_2$(XPhos)] (**7**) in $CDCl_3$.

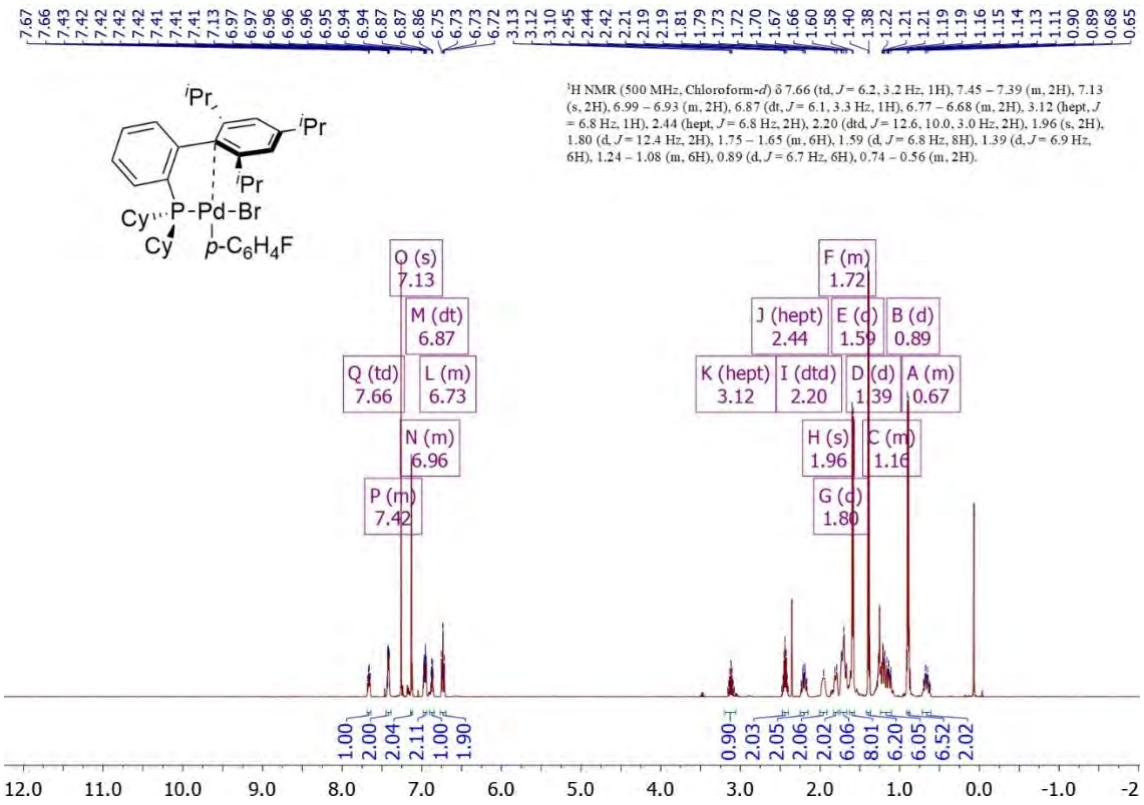


Figure ESI17. ^{1}H NMR of [PdBr(*p*-C_6H_4F)(XPhos)] (**9**) in $CDCl_3$.

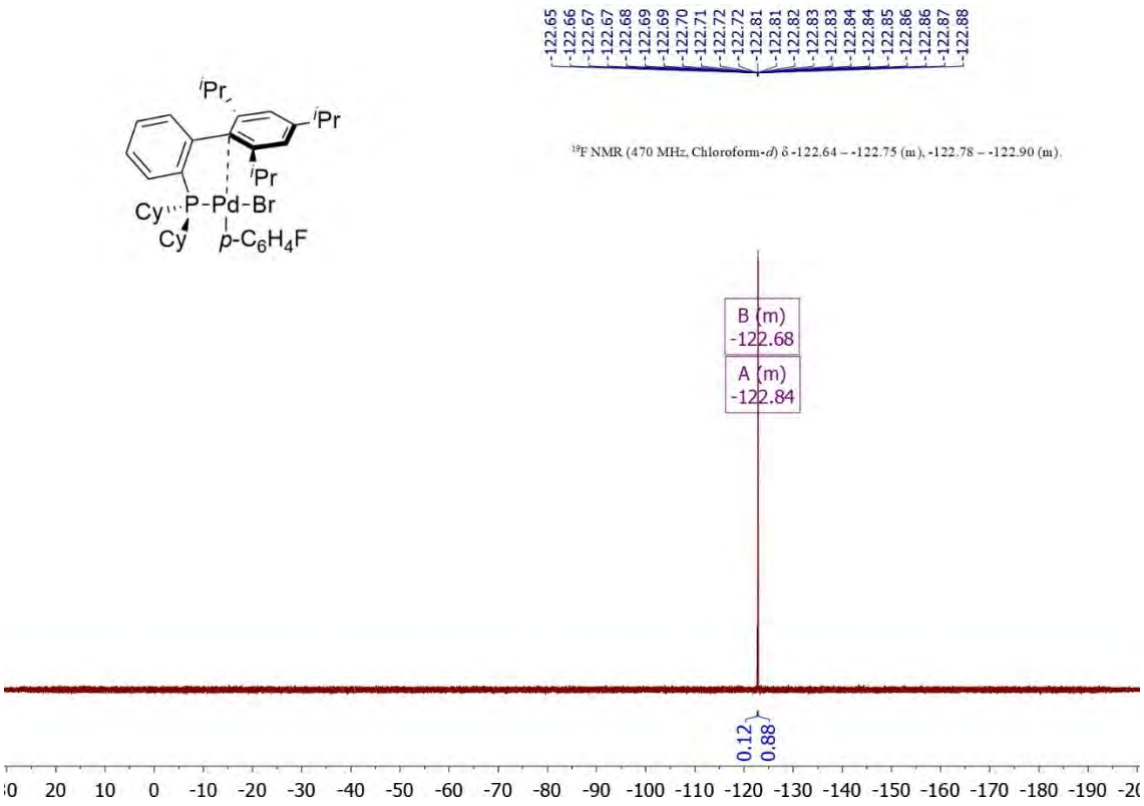


Figure ESI18. ^{19}F NMR of [PdBr(*p*-C_6H_4F)(XPhos)] (**9**) in $CDCl_3$.

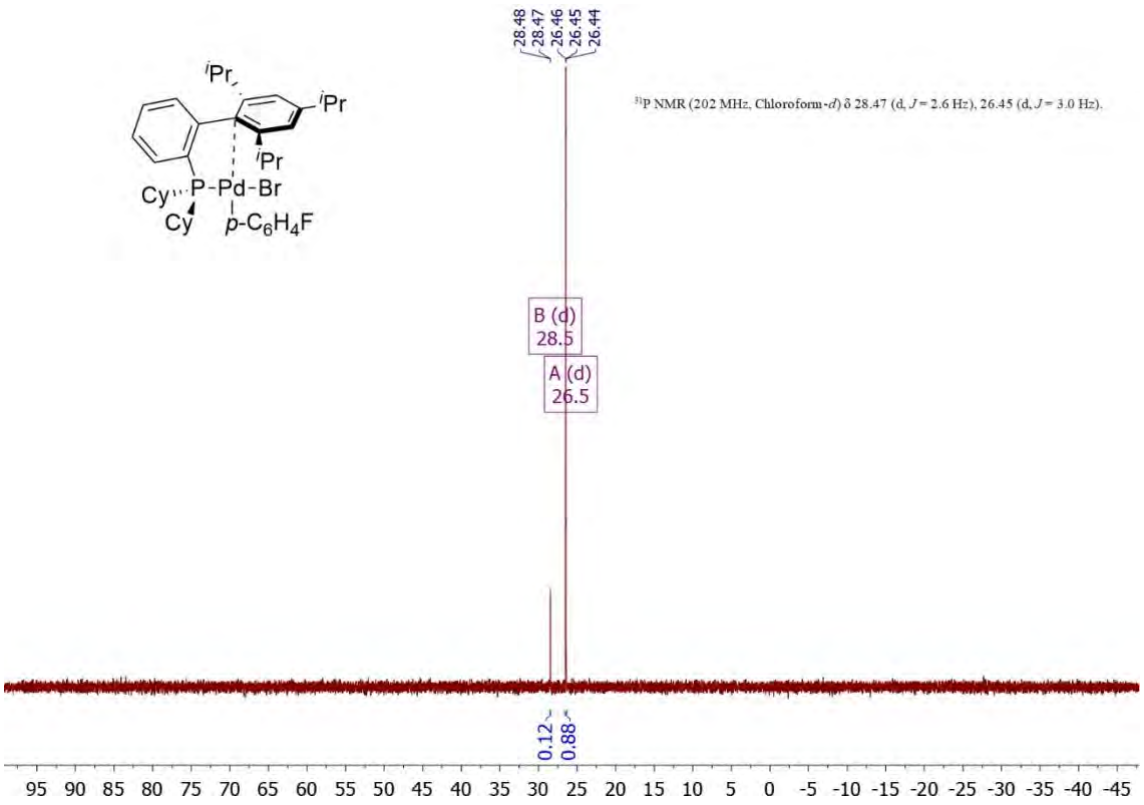


Figure ESI19. $^{31}P\{^1H\}$ NMR of [PdBr(*p*-C_6H_4F)(XPhos)] (**9**) in $CDCl_3$.

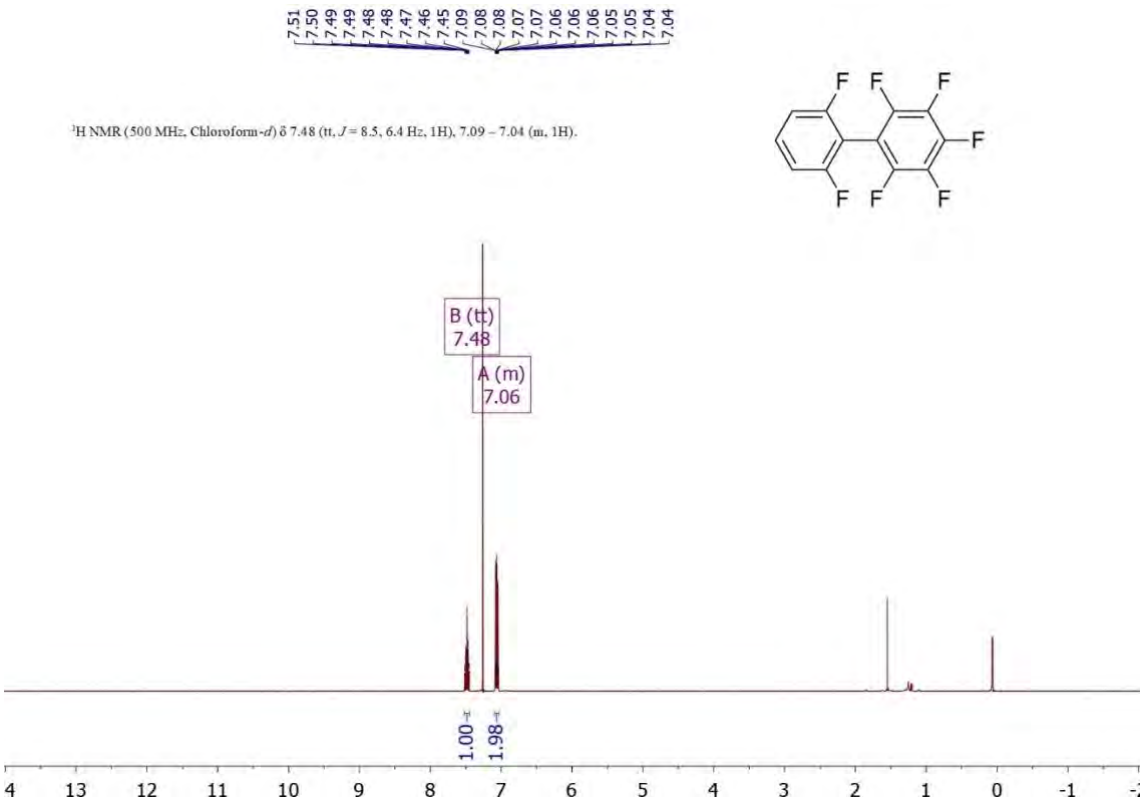


Figure ESI20. ^{1}H NMR of 2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl (**3an**) in $CDCl_3$.

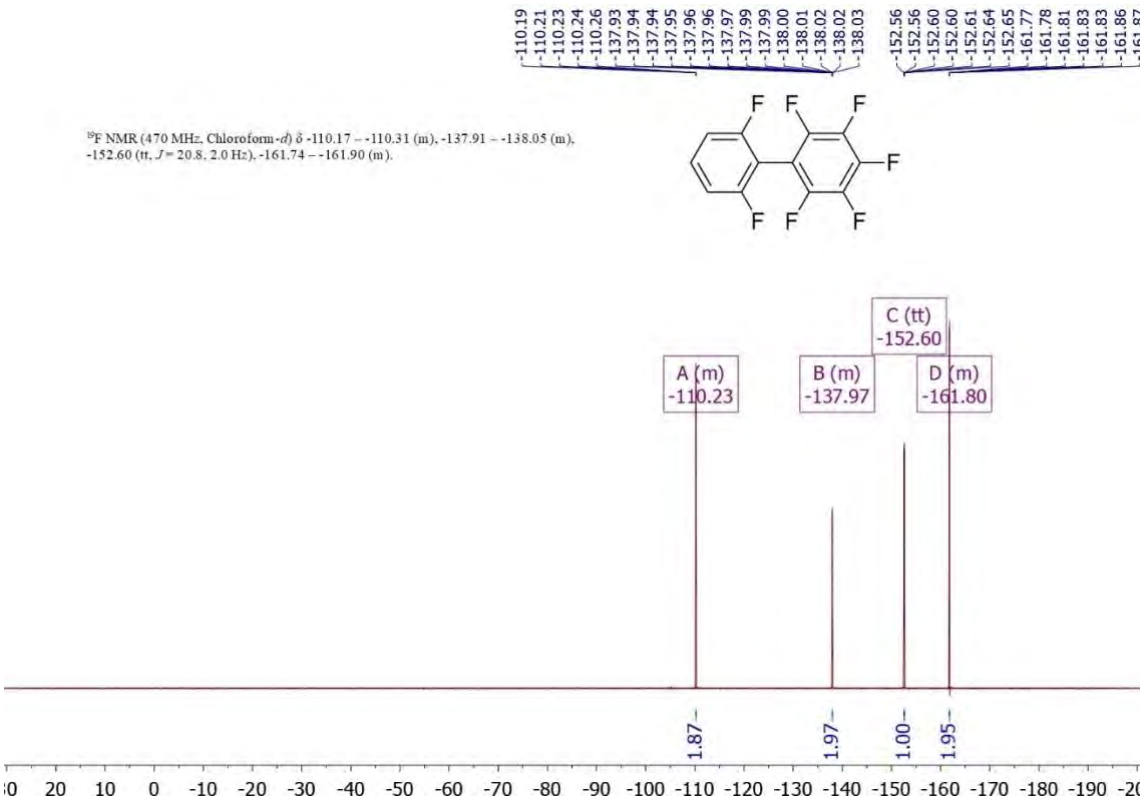


Figure ESI21. ^{19}F NMR of 2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl (**3an**) in $CDCl_3$.

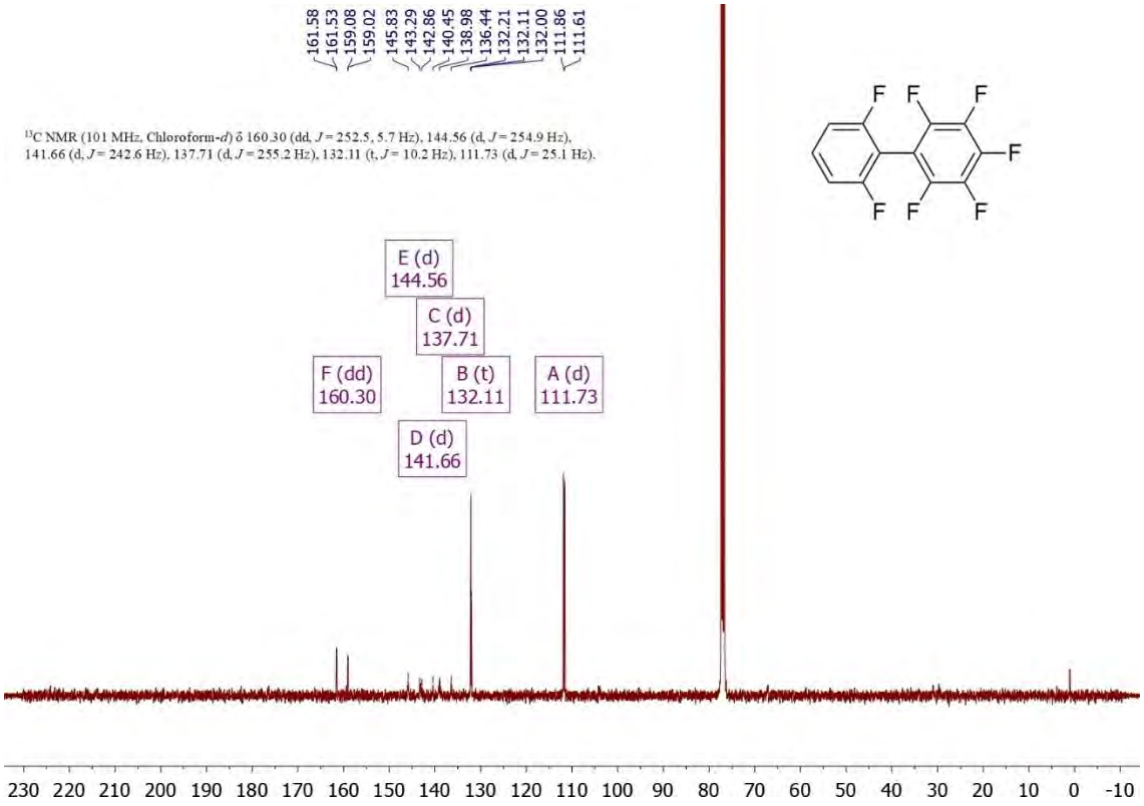


Figure ESI22. $^{13}C\{^{1}H\}$ NMR of 2,2',3,4,5,6,6'-heptafluoro-1,1'-biphenyl (**3an**) in $CDCl_3$.

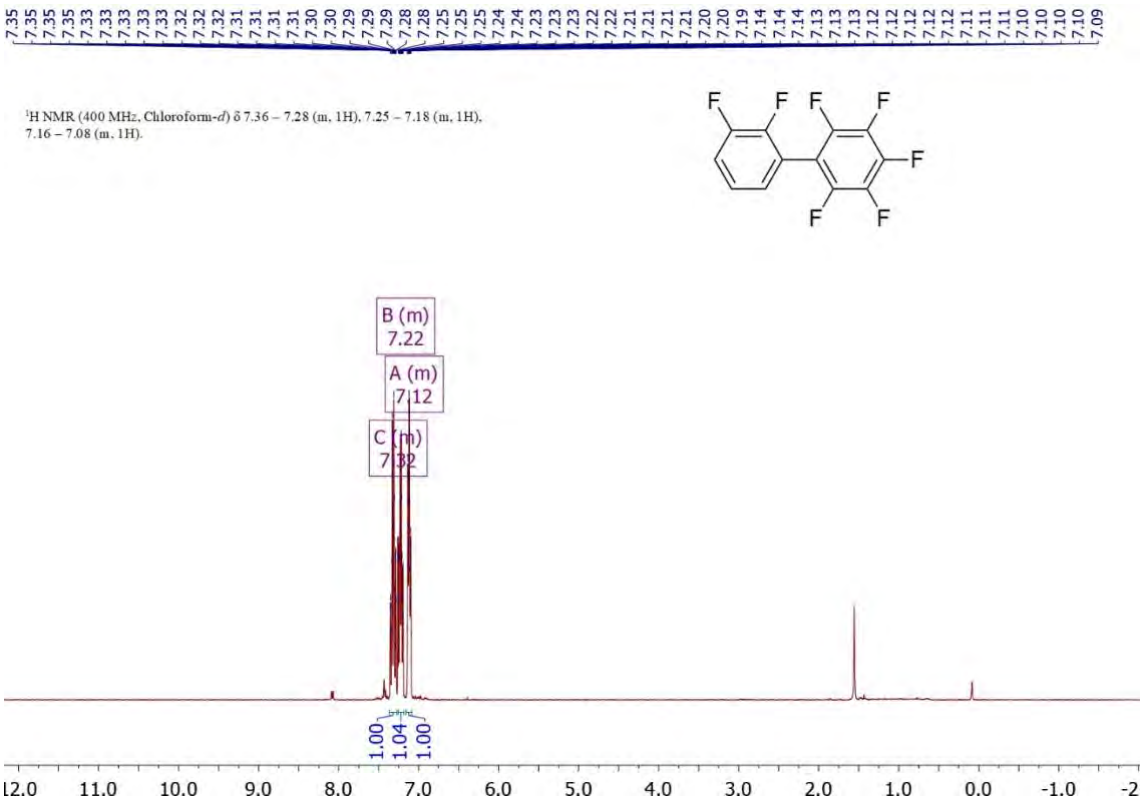


Figure ESI23. ^{1}H NMR of 2,2',3,3',4,5,6-heptafluoro-1,1'-biphenyl (**3bn**) in $CDCl_3$.

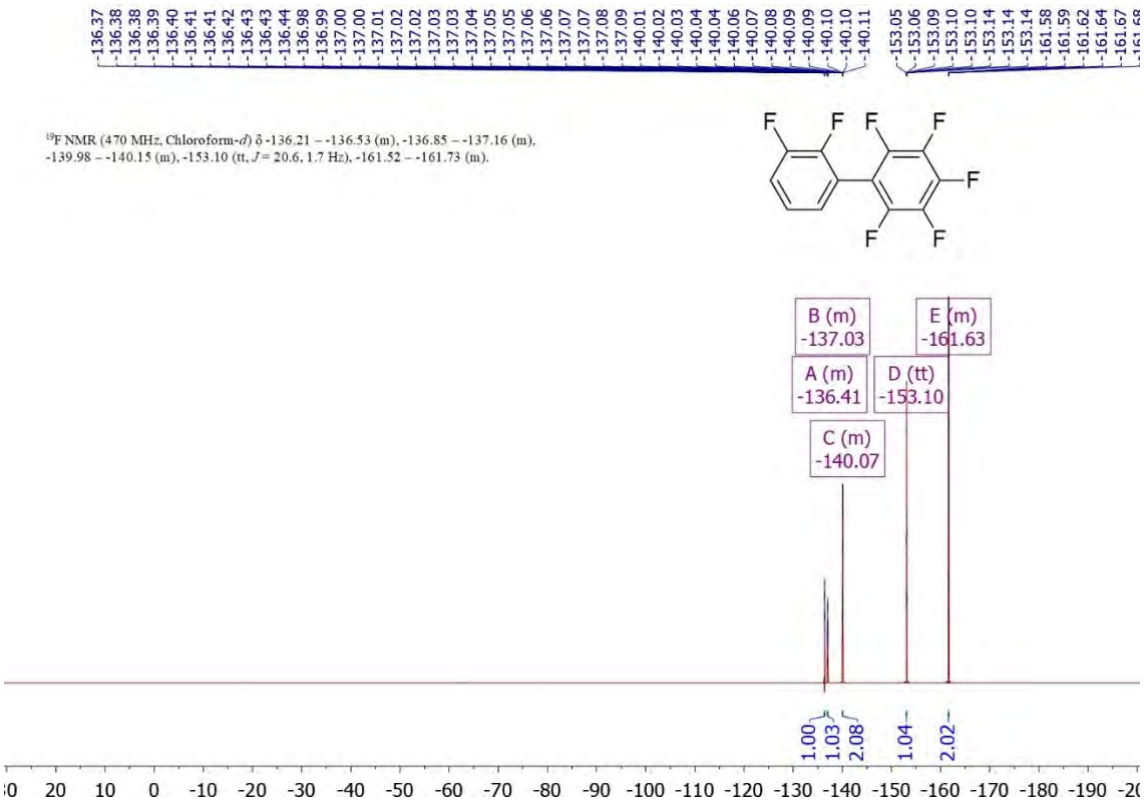


Figure ESI24. ^{19}F NMR of 2,2',3,3',4,5,6-heptafluoro-1,1'-biphenyl (**3bn**) in $CDCl_3$.

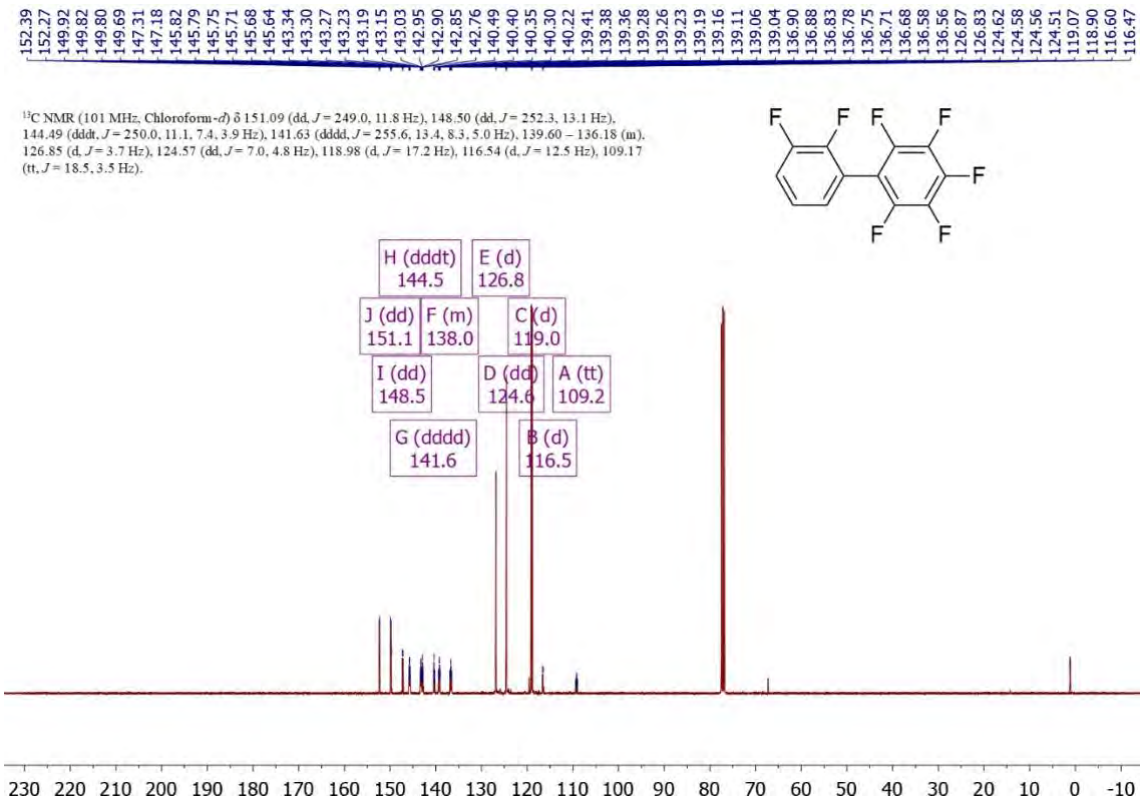


Figure 25. $^{13}C\{^1H\}$ NMR of 2,2',3,3',4,5,6-heptafluoro-1,1'-biphenyl (**3bn**) in $CDCl_3$.

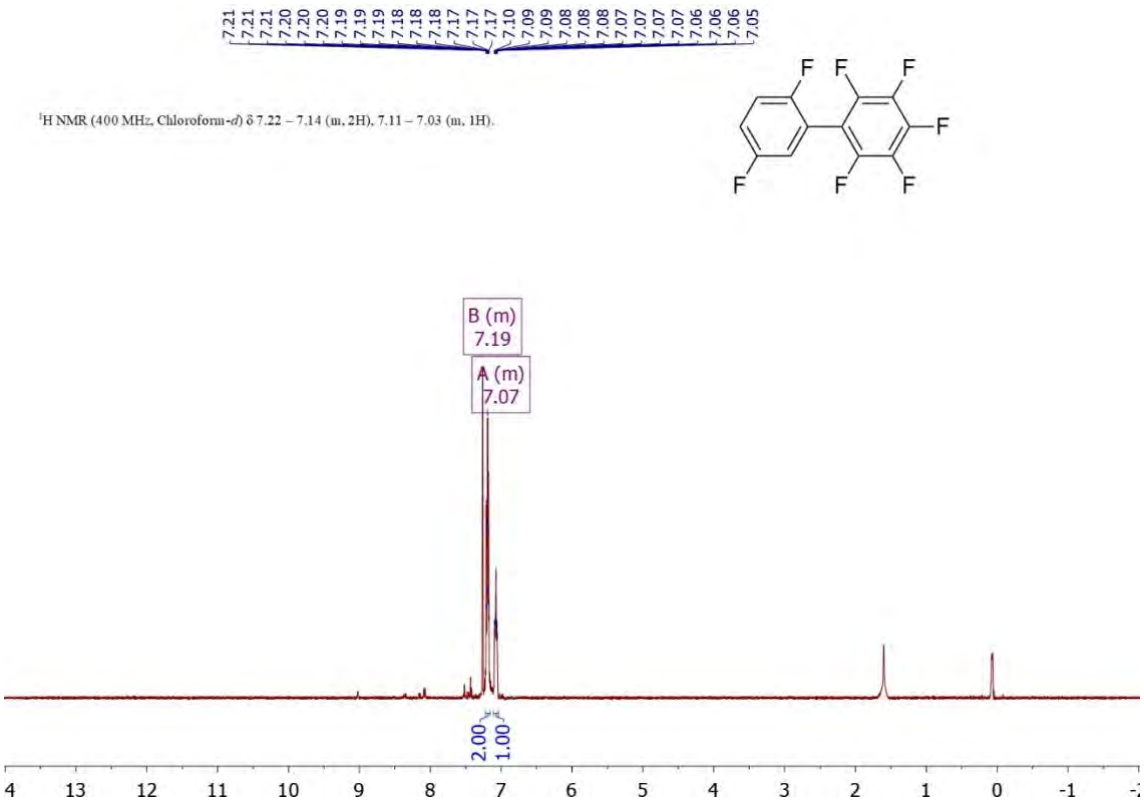


Figure ESI26. ^{1}H NMR of 2,2',3,4,5,5',6-heptafluoro-1,1'-biphenyl (**3cn**) in $CDCl_3$.

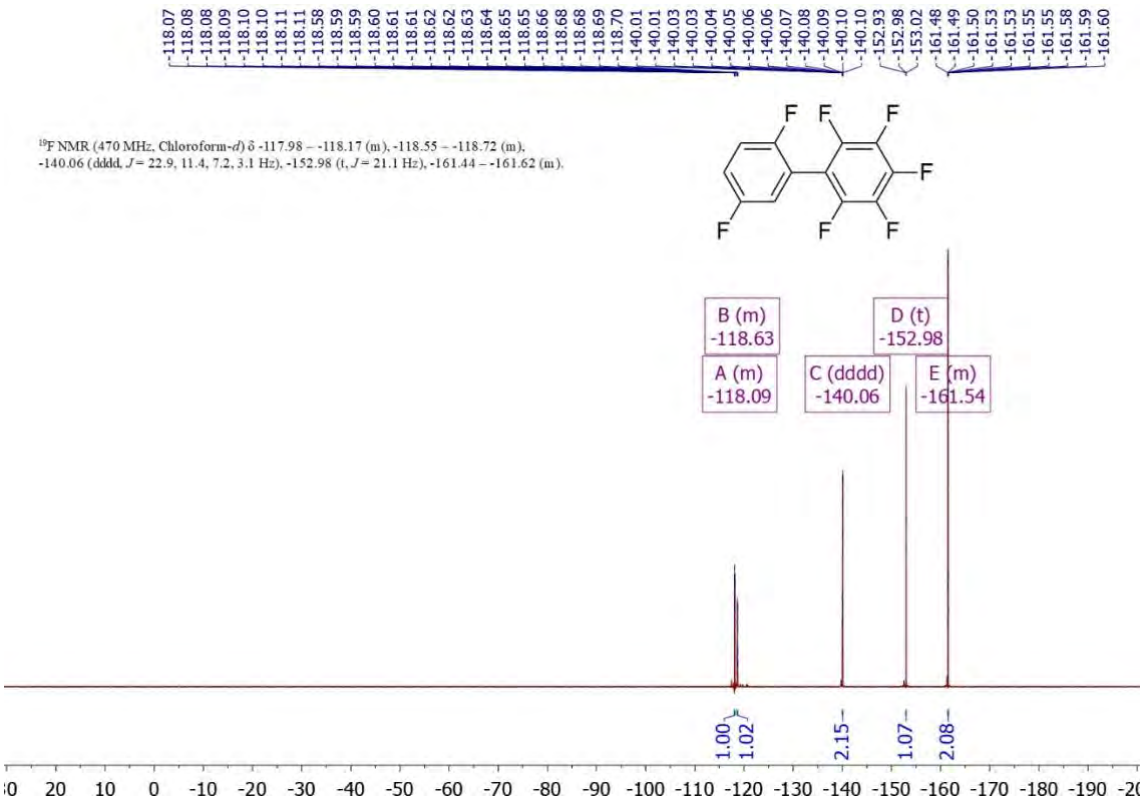


Figure ESI27. ^{19}F NMR of 2,2',3,4,5,5',6-heptafluoro-1,1'-biphenyl (**3cn**) in $CDCl_3$.

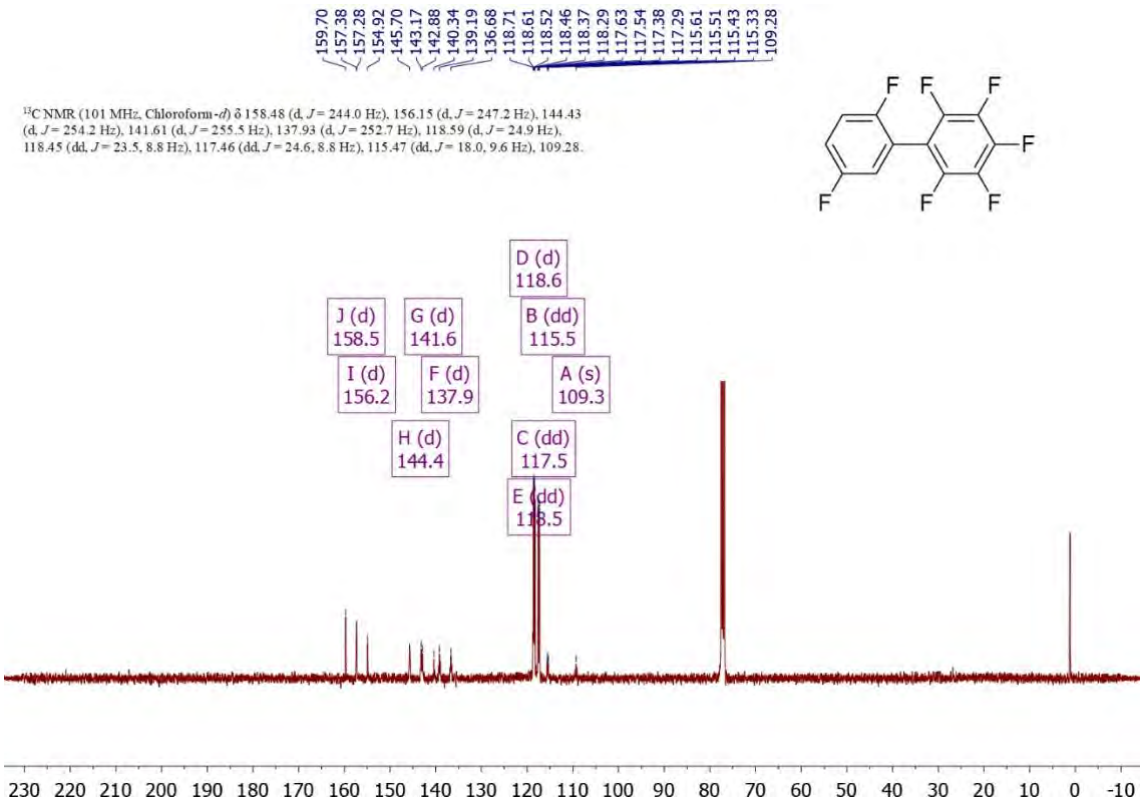


Figure ESI28. $^{13}C\{^{1}H\}$ NMR of 2,2',3,4,5,5',6-heptafluoro-1,1'-biphenyl (**3cn**) in $CDCl_3$.

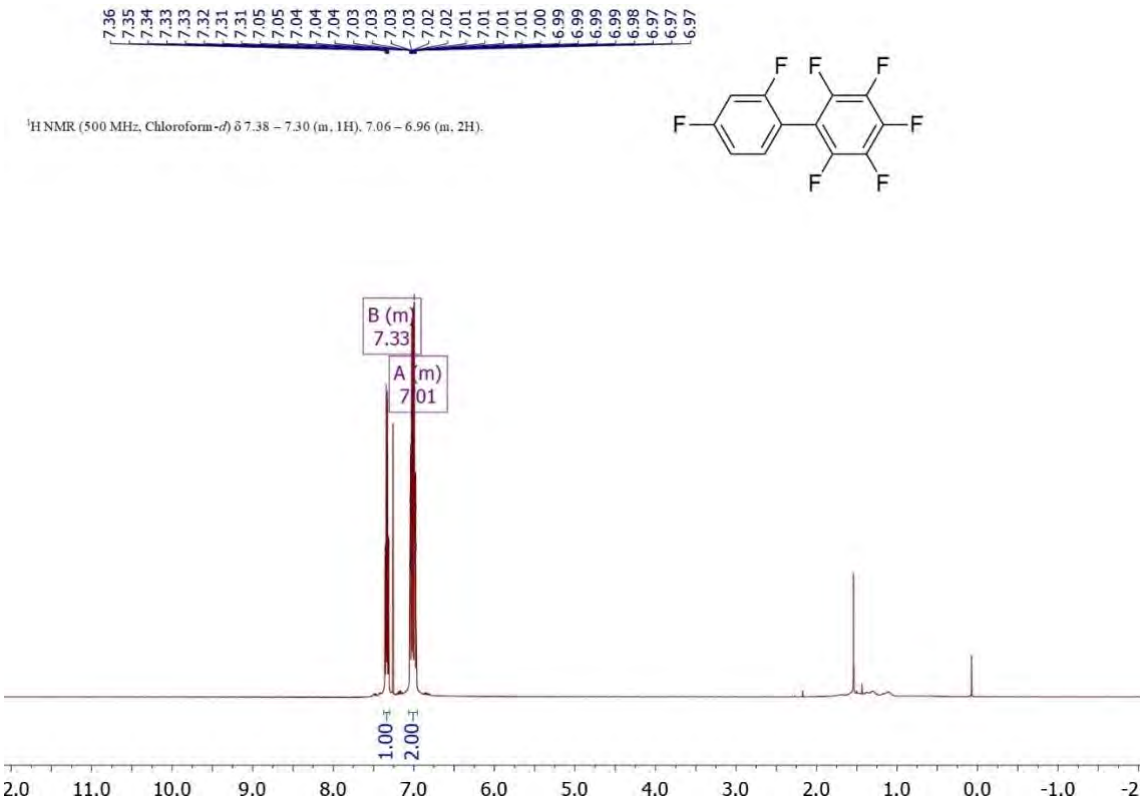


Figure ESI29. ^{1}H NMR of 2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl (**3dn**) in $CDCl_3$.

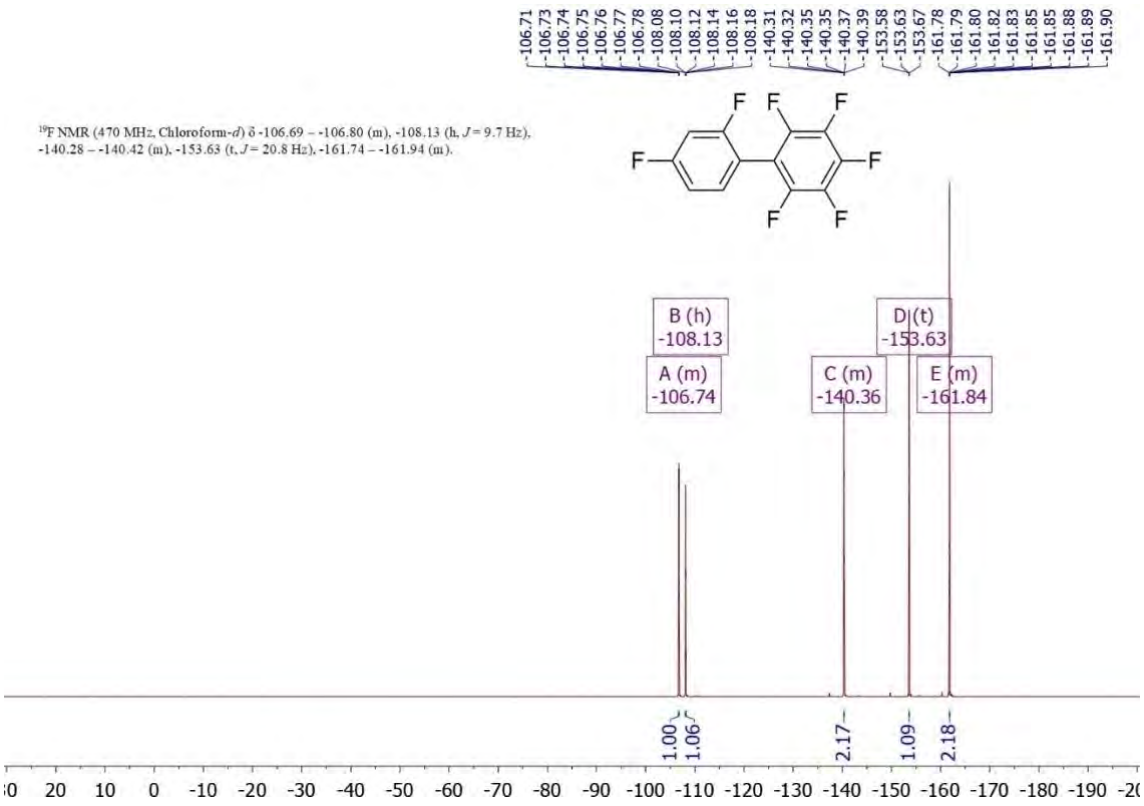


Figure ESI30. ^{19}F NMR of 2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl (**3dn**) in $CDCl_3$.

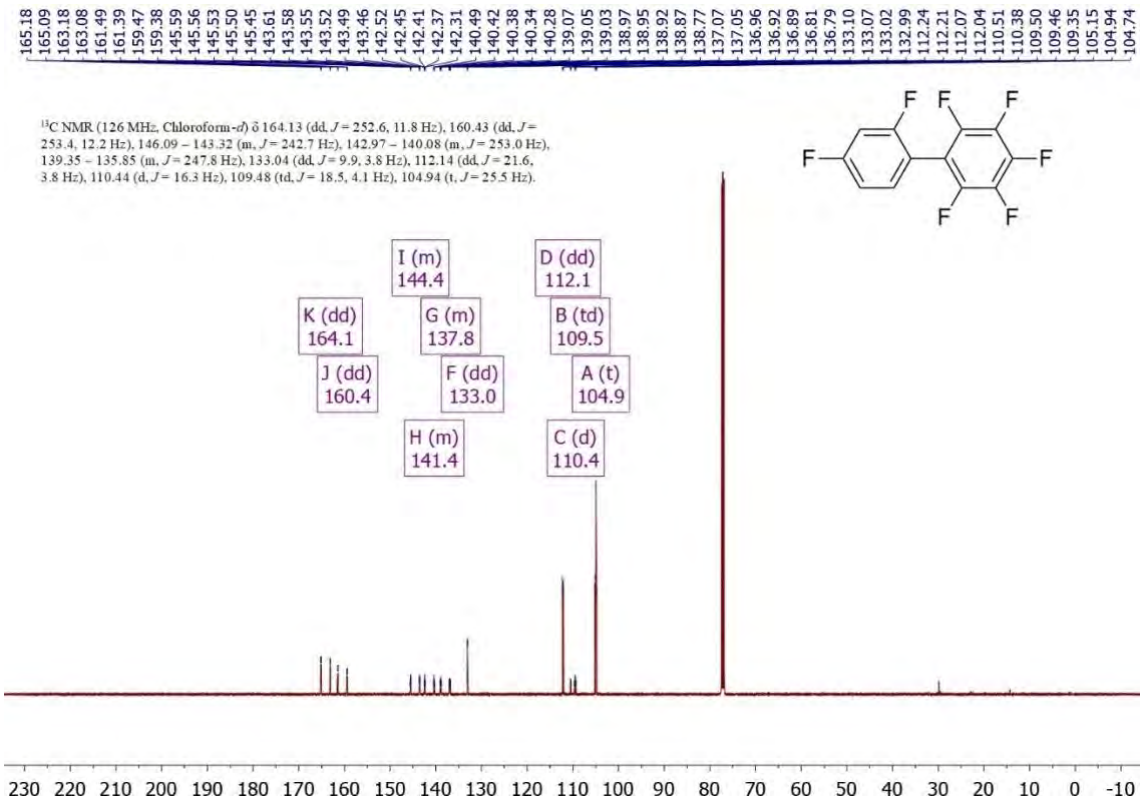


Figure ESI31. $^{13}C\{^1H\}$ NMR of 2,2',3,4,4',5,6-heptafluoro-1,1'-biphenyl (**3dn**) in $CDCl_3$.

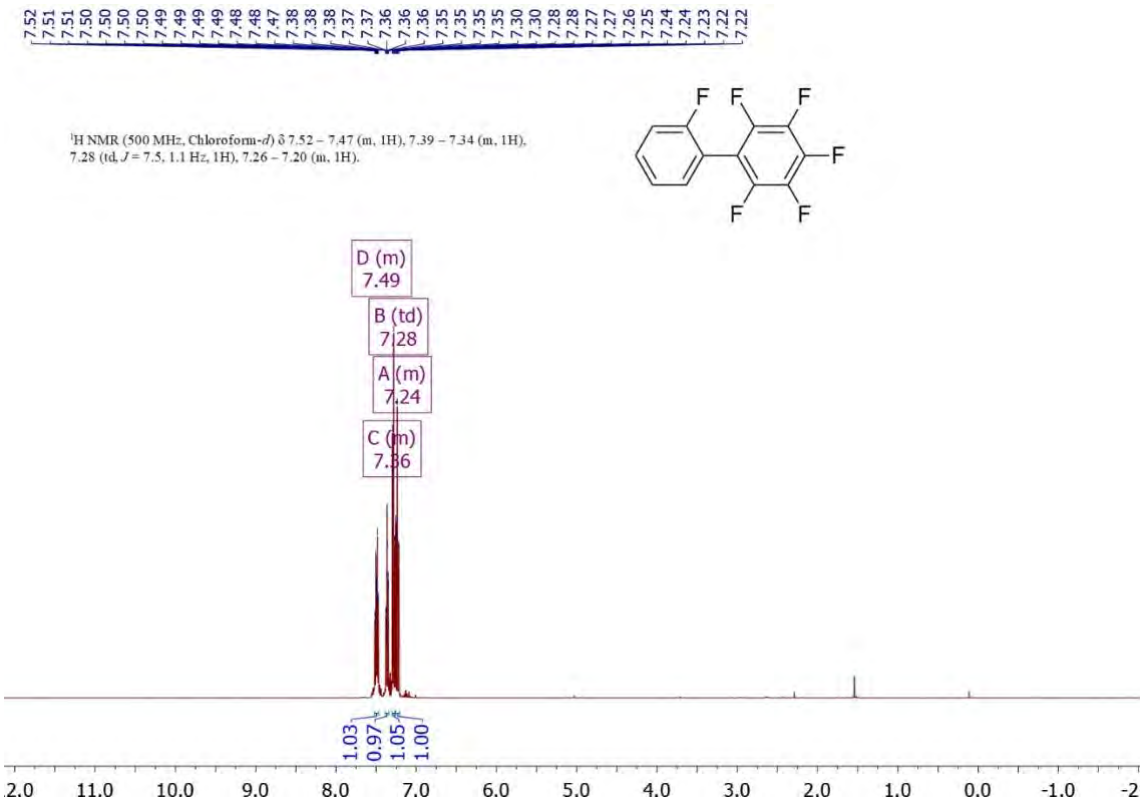


Figure ESI32. ^{1}H NMR of 2,2',3,4,5,6-heptafluoro-1,1'-biphenyl (**3en**) in $CDCl_3$.

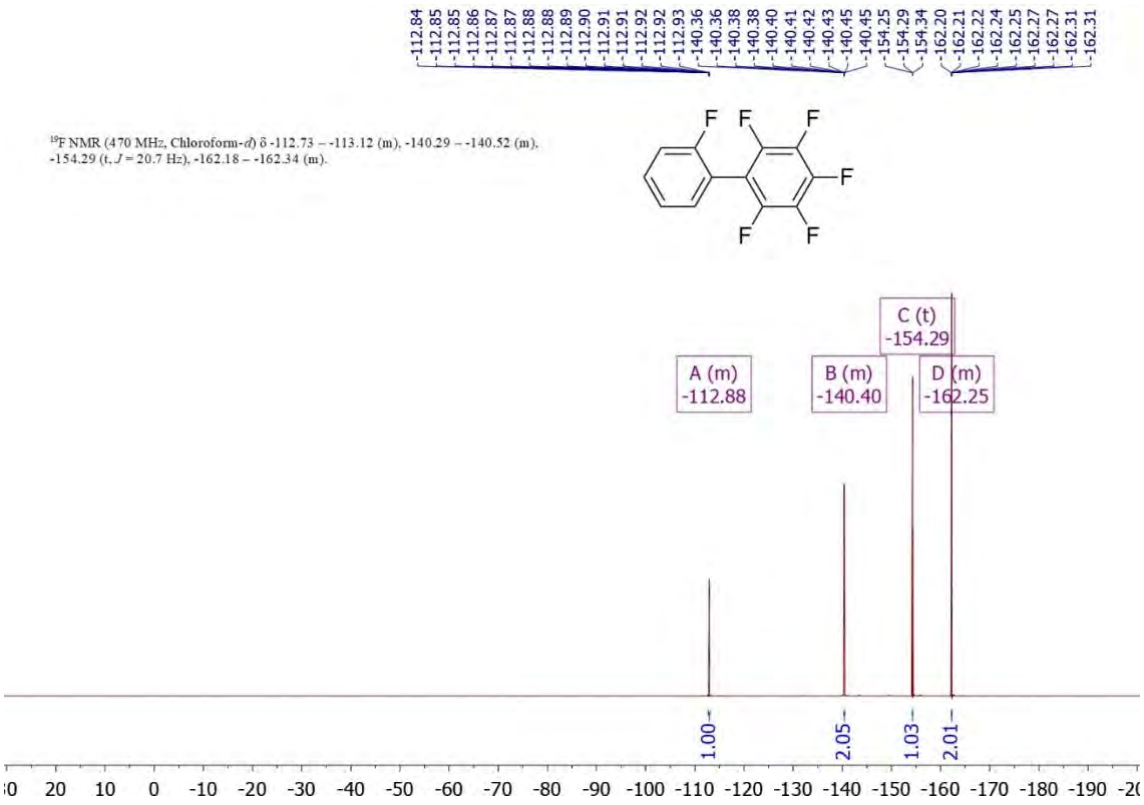


Figure ESI33. ^{19}F NMR of 2,2',3,4,5,6-heptafluoro-1,1'-biphenyl (**3en**) in $CDCl_3$.

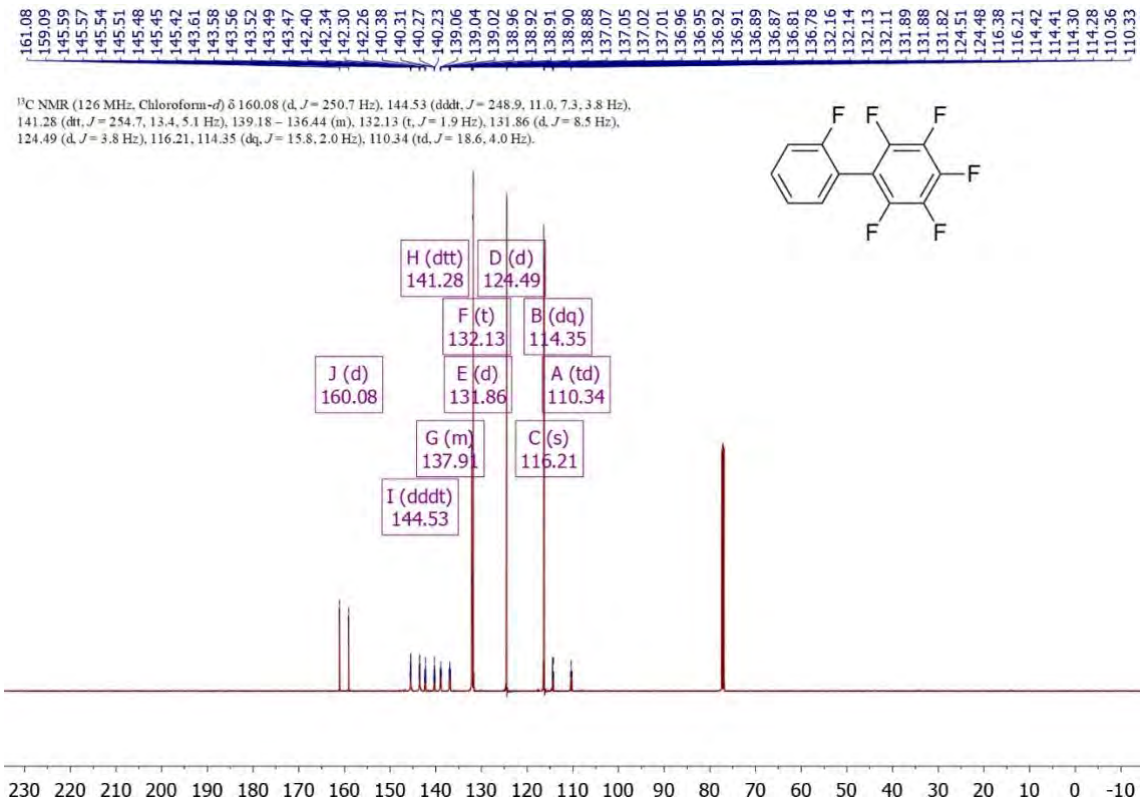


Figure ESI34. $^{13}C\{^{1}H\}$ NMR of 2,2',3,4,5,6-heptafluoro-1,1'-biphenyl (**3en**) in $CDCl_3$.

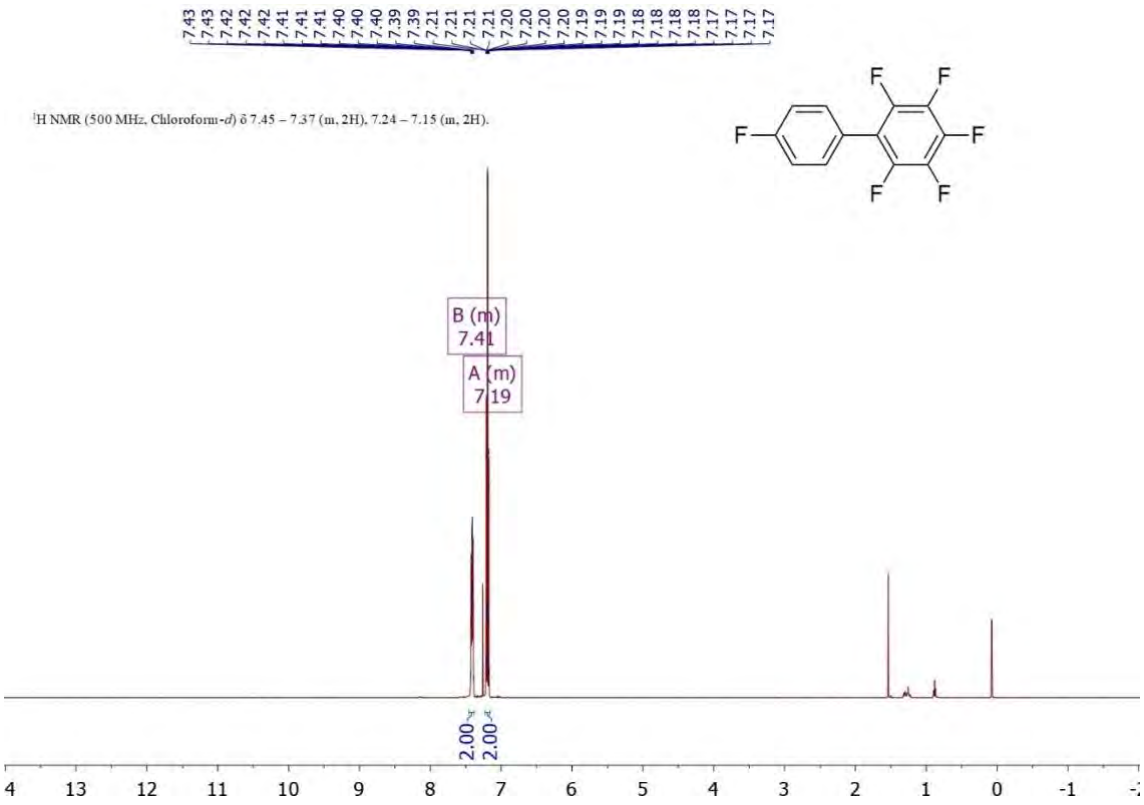


Figure ESI35. ^{1}H NMR of 2,3,4,4',5,6-hexafluoro-1,1'-biphenyl (**3fn**) in $CDCl_3$.

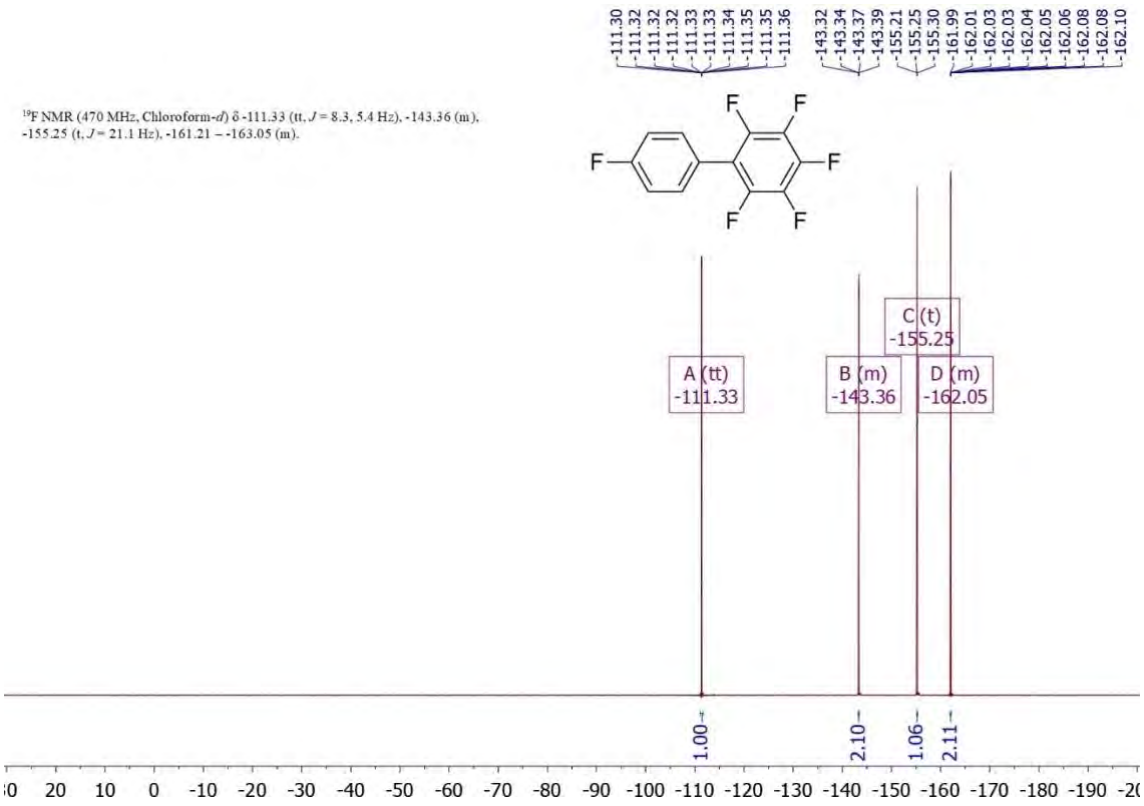


Figure ESI36. ^{19}F NMR of 2,3,4,4',5,6-hexafluoro-1,1'-biphenyl (**3fn**) in $CDCl_3$.

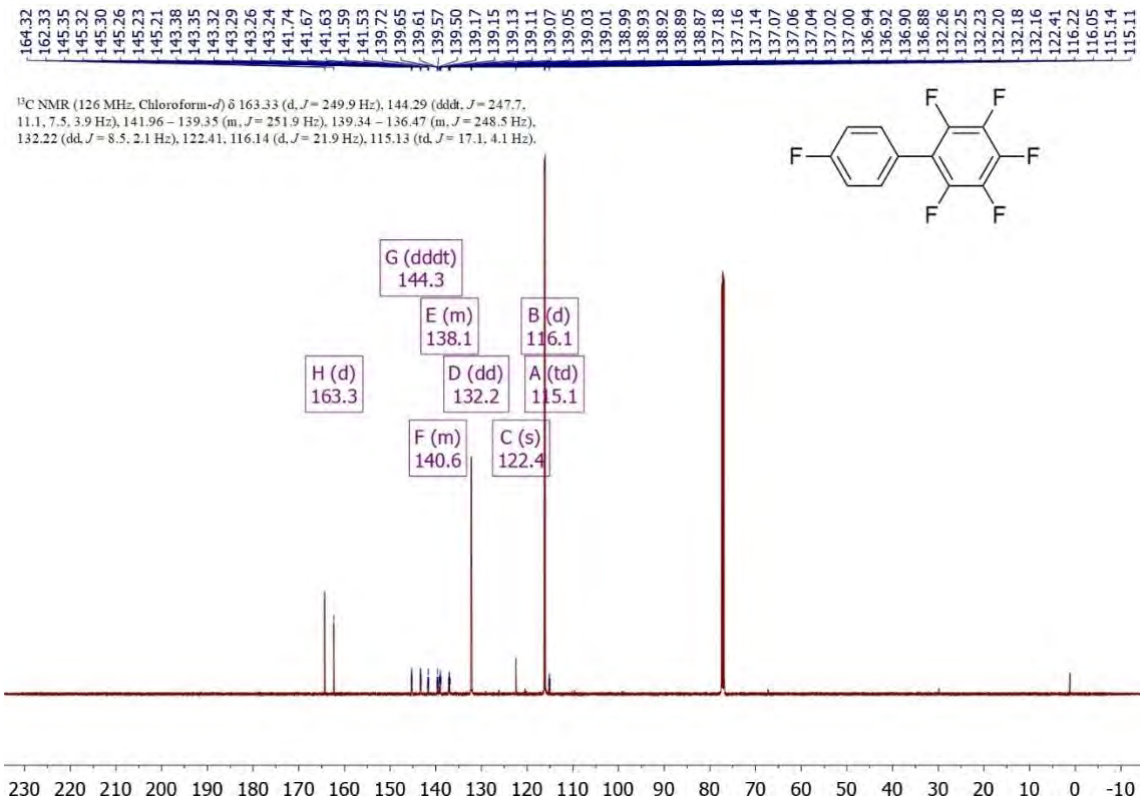


Figure ESI37. $^{13}C\{^1H\}$ NMR of 2,3,4,4',5,6-hexafluoro-1,1'-biphenyl (**3fn**) in $CDCl_3$.

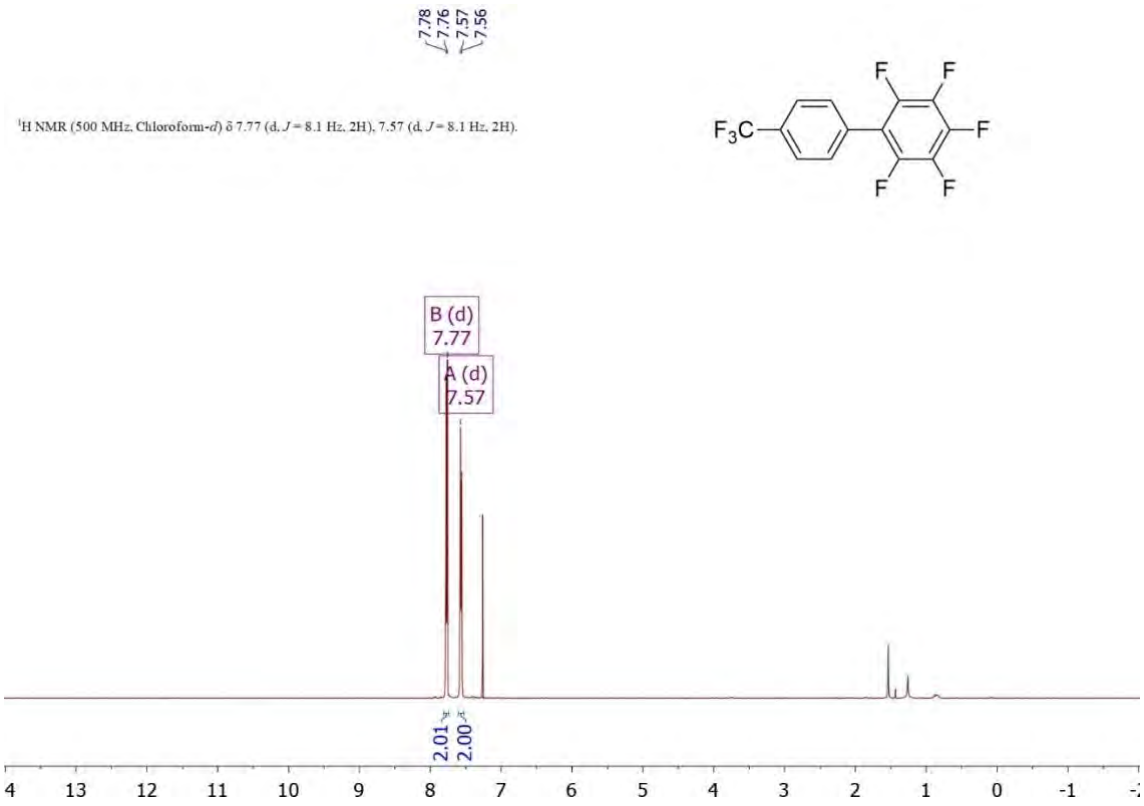


Figure ESI38. ^{1}H NMR of 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl (**3gn**) in $CDCl_3$.

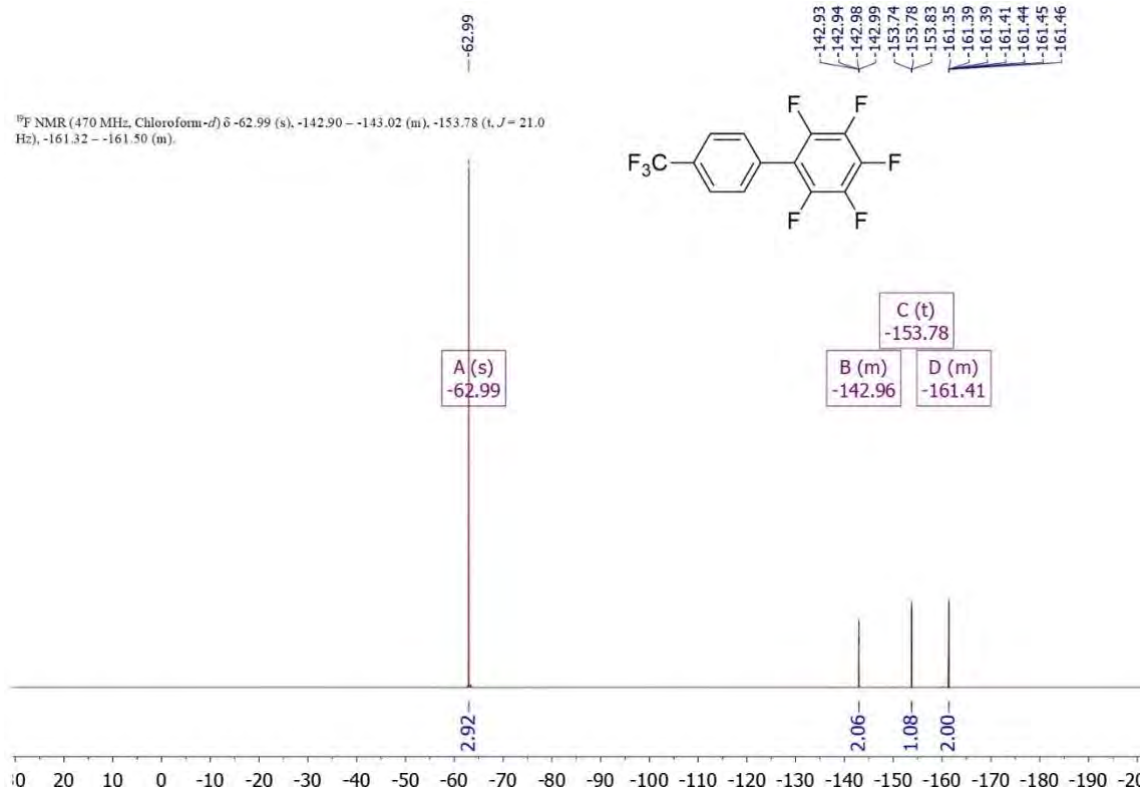


Figure ESI39. ^{19}F NMR of 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl (**3gn**) in $CDCl_3$.

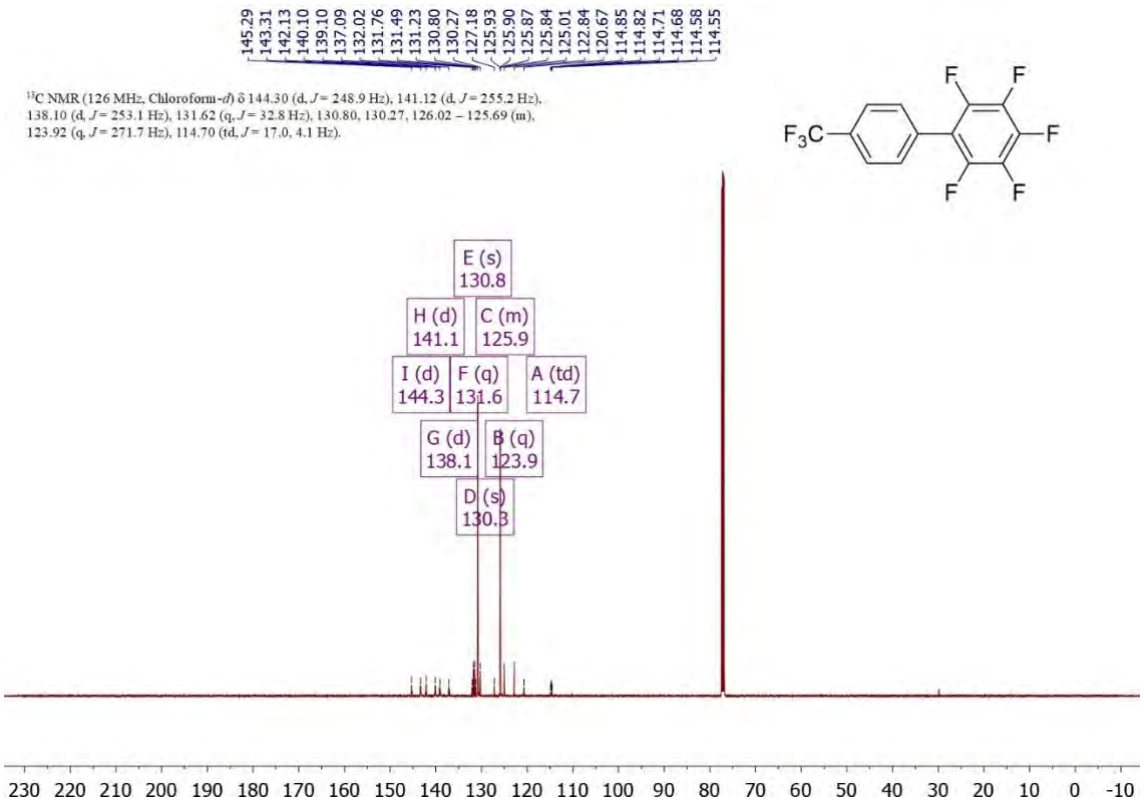


Figure ESI40. $^{13}C\{^{1}H\}$ NMR of 2,3,4,5,6-pentafluoro-4'-(trifluoromethyl)-1,1'-biphenyl (**3gn**) in $CDCl_3$.

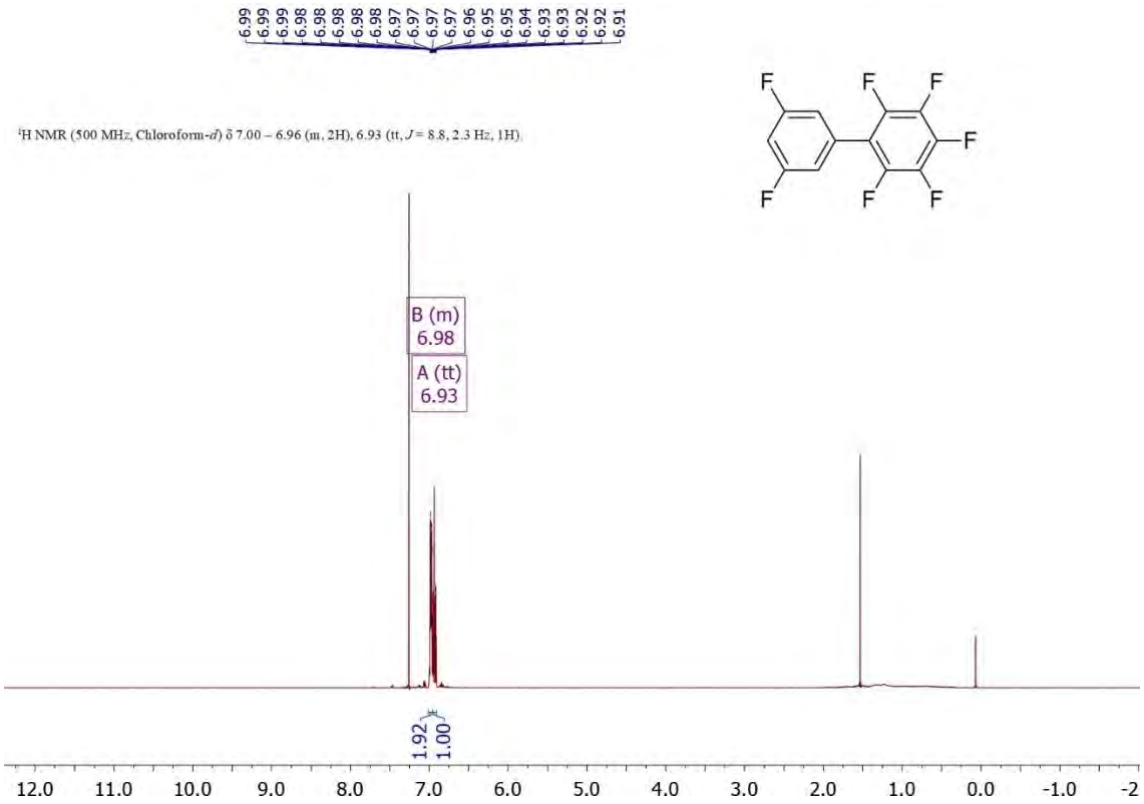


Figure ESI41. ^{1}H NMR of 2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl (**3hn**) in $CDCl_3$.

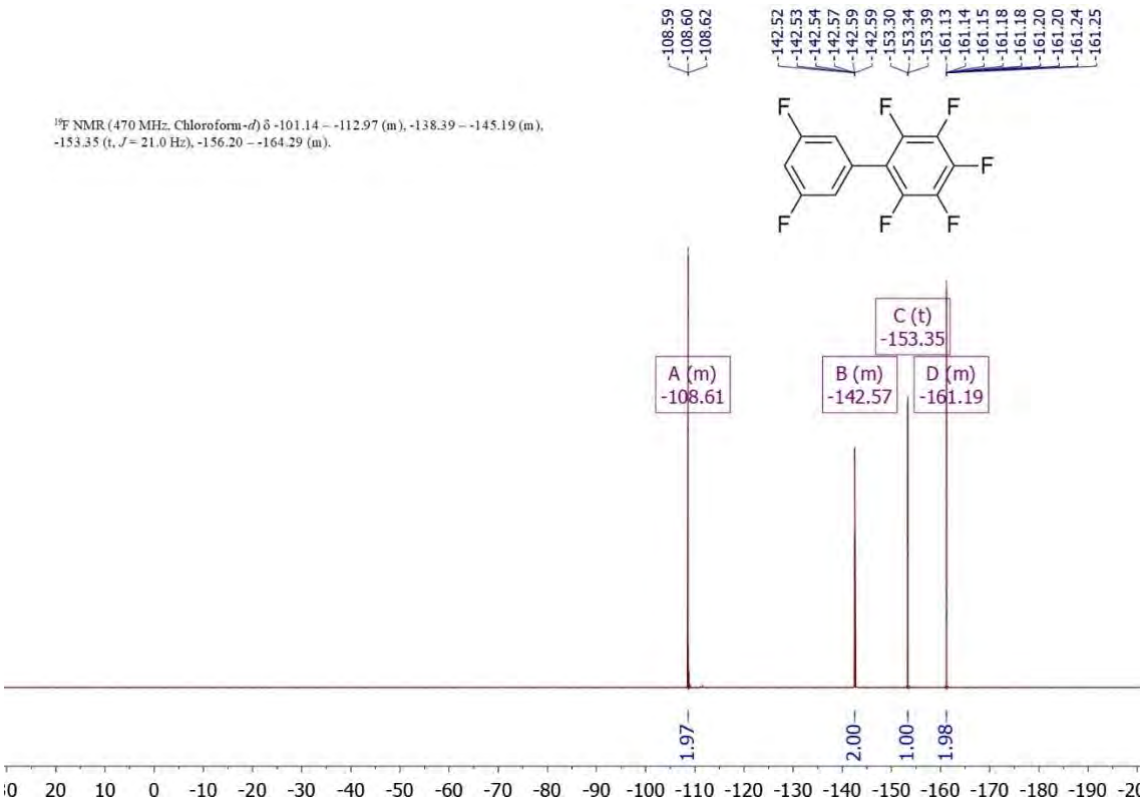


Figure ESI42. ^{19}F NMR of 2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl (**3hn**) in $CDCl_3$.

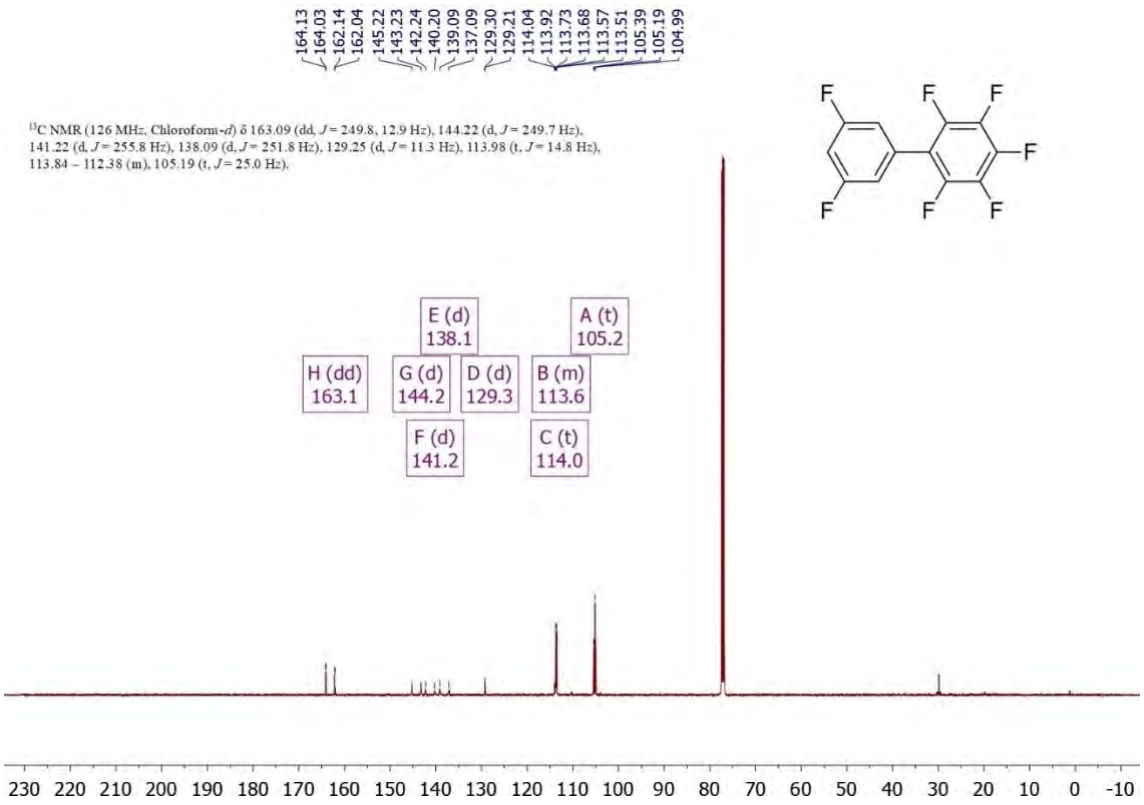


Figure ESI43. $^{13}C\{^1H\}$ NMR of 2,3,3',4,5,5',6-heptafluoro-1,1'-biphenyl (**3hn**) in $CDCl_3$.

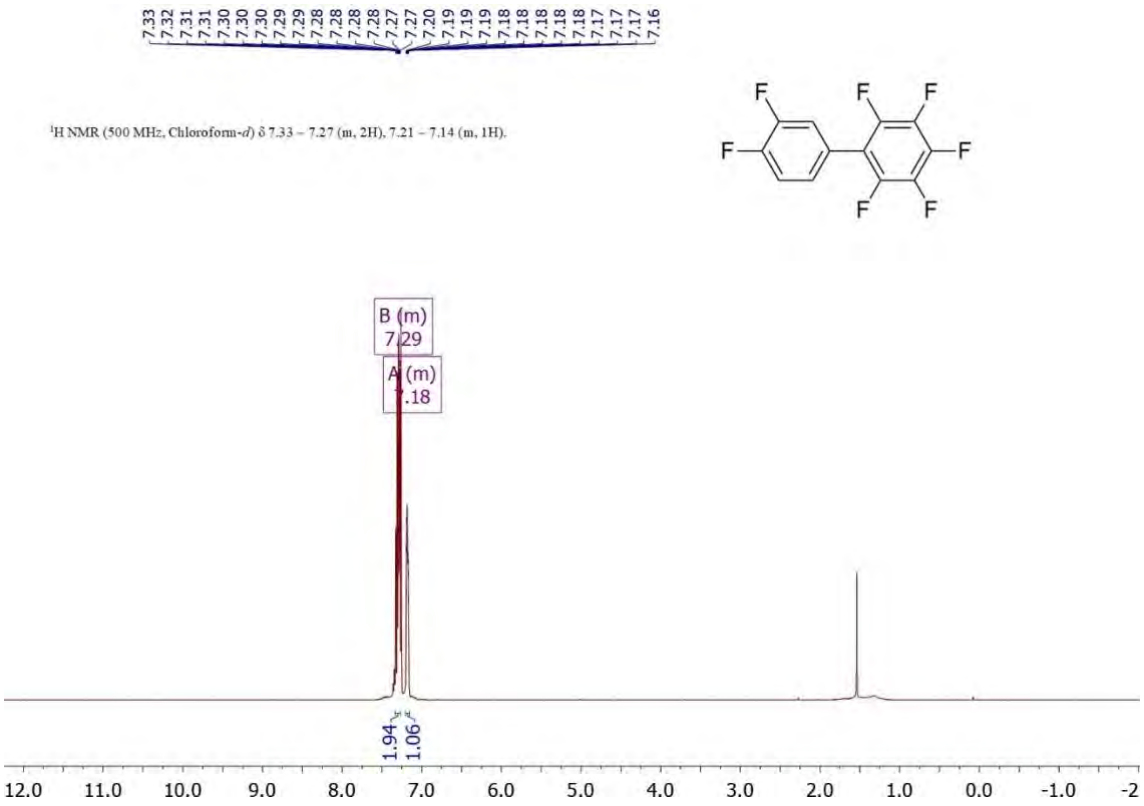


Figure ESI44. ^{1}H NMR of 2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl (**3in**) in $CDCl_3$.

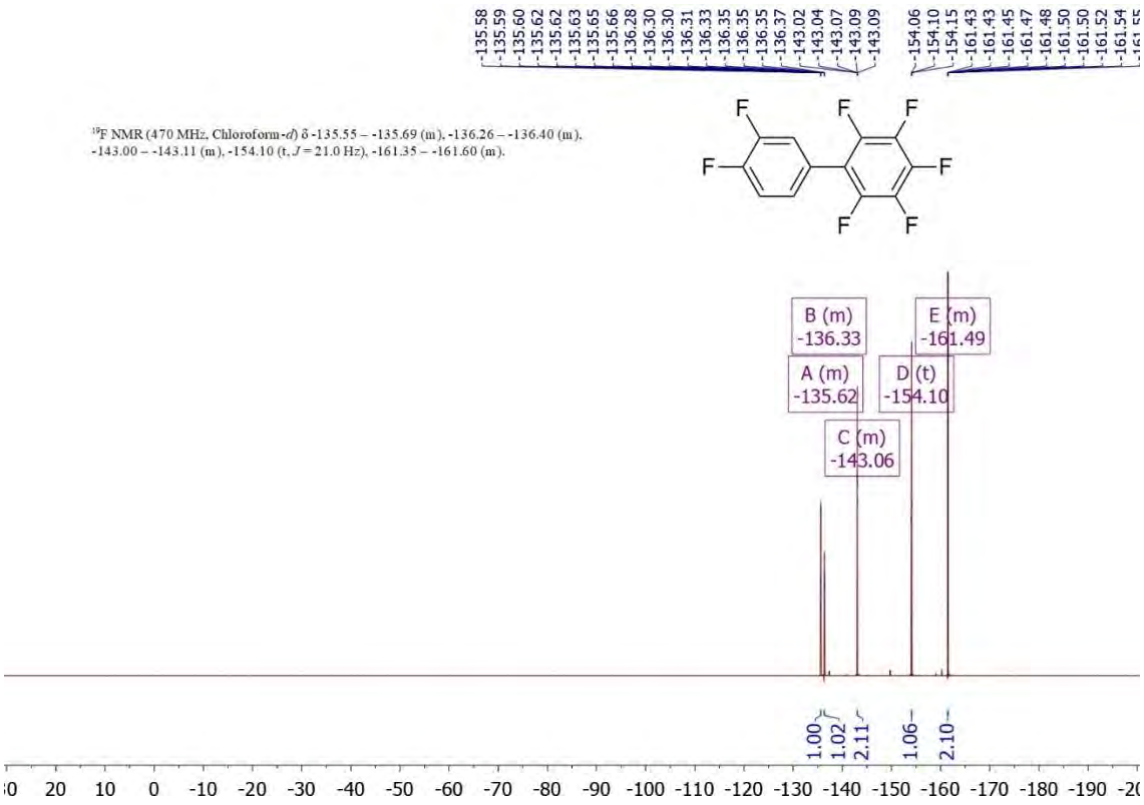


Figure ESI45. ^{19}F NMR of 2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl (**3in**) in $CDCl_3$.

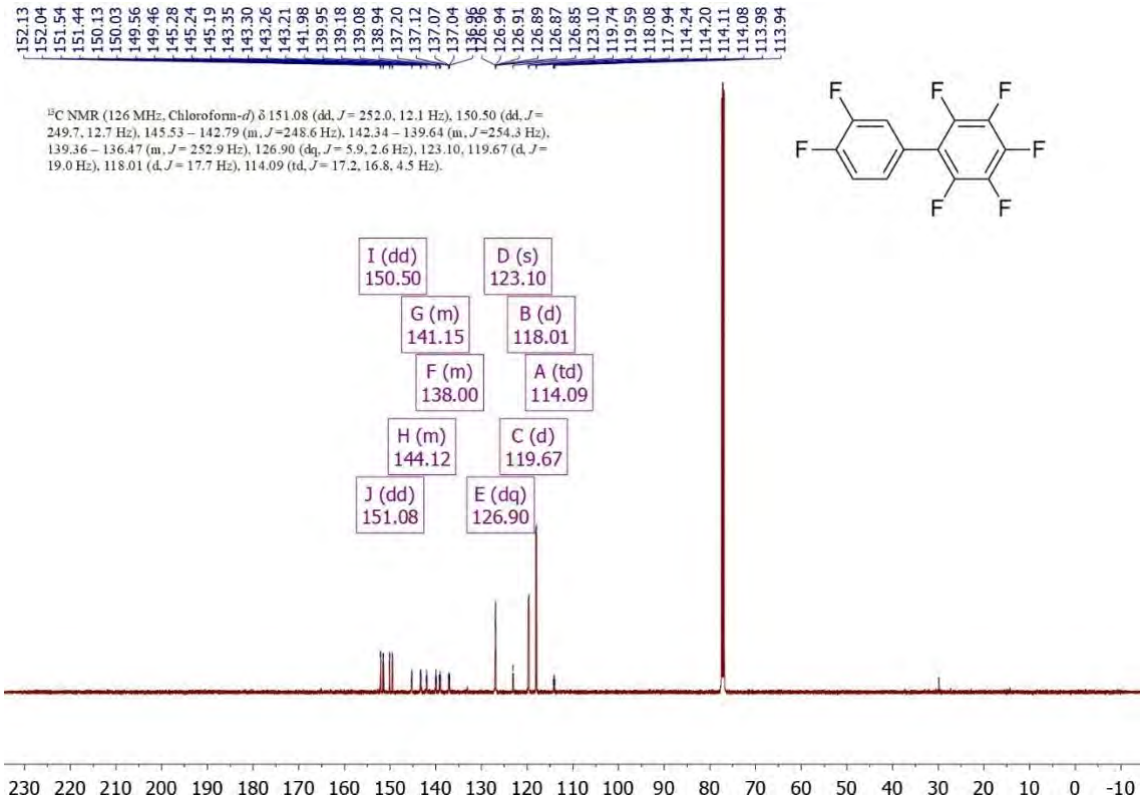


Figure ESI46. $^{13}C\{^{1}H\}$ NMR of 2,3,3',4,4',5,6-heptafluoro-1,1'-biphenyl (**3in**) in $CDCl_3$.

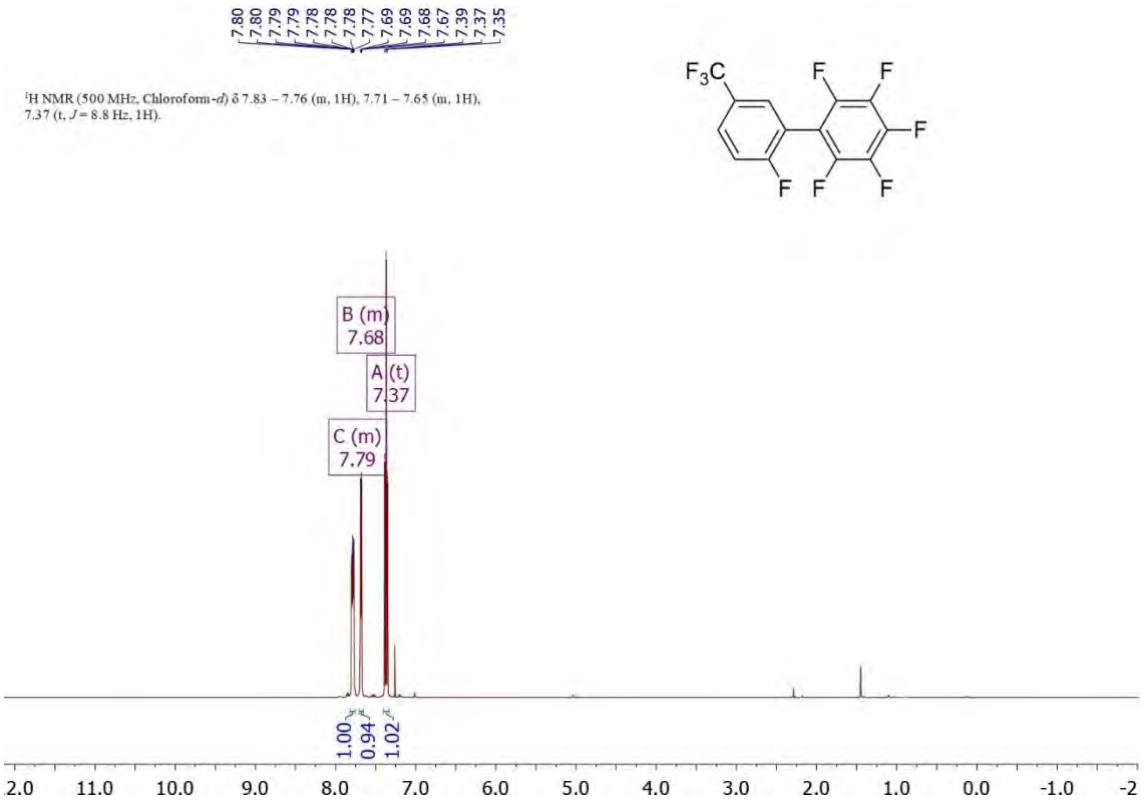


Figure ESI47. ^{1}H NMR of 2,2',3,4,5,6-hexafluoro-5'-(trifluoromethyl)-1,1'-biphenyl (**3jn**) in $CDCl_3$.

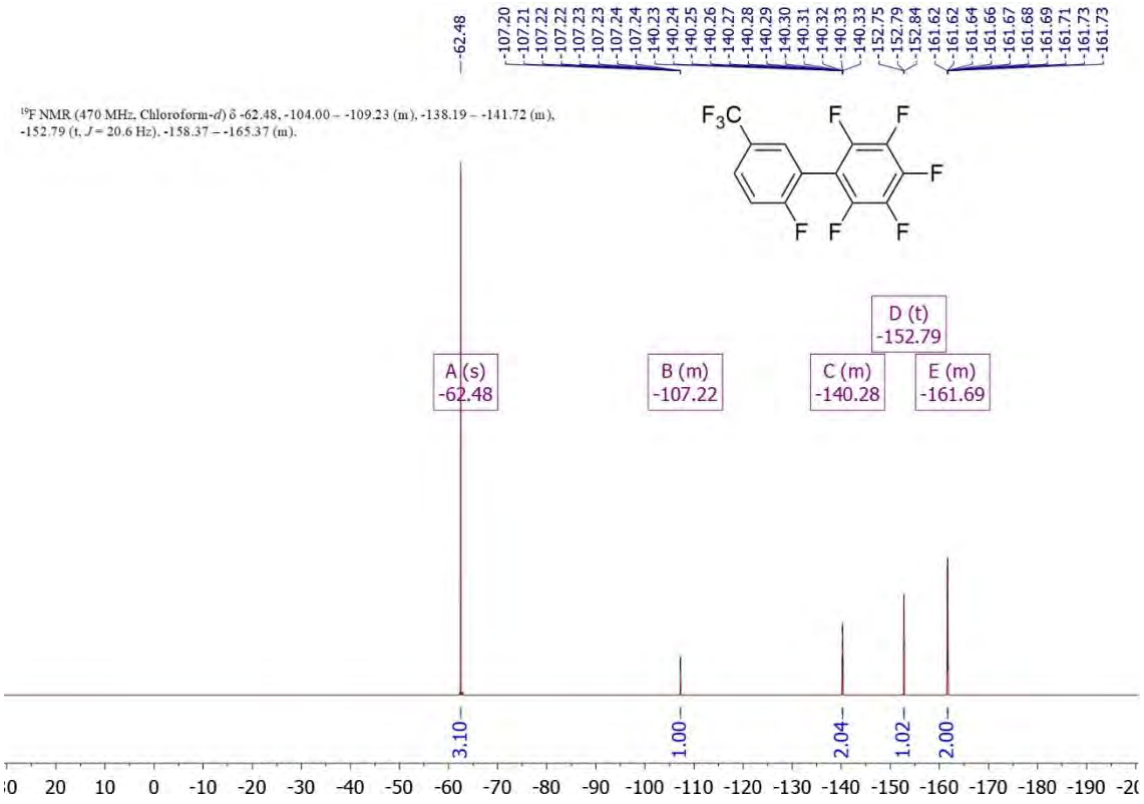


Figure ESI48. ^{19}F NMR of 2,2',3,4,5,6-hexafluoro-5'-(trifluoromethyl)-1,1'-biphenyl (**3jn**) in $CDCl_3$.

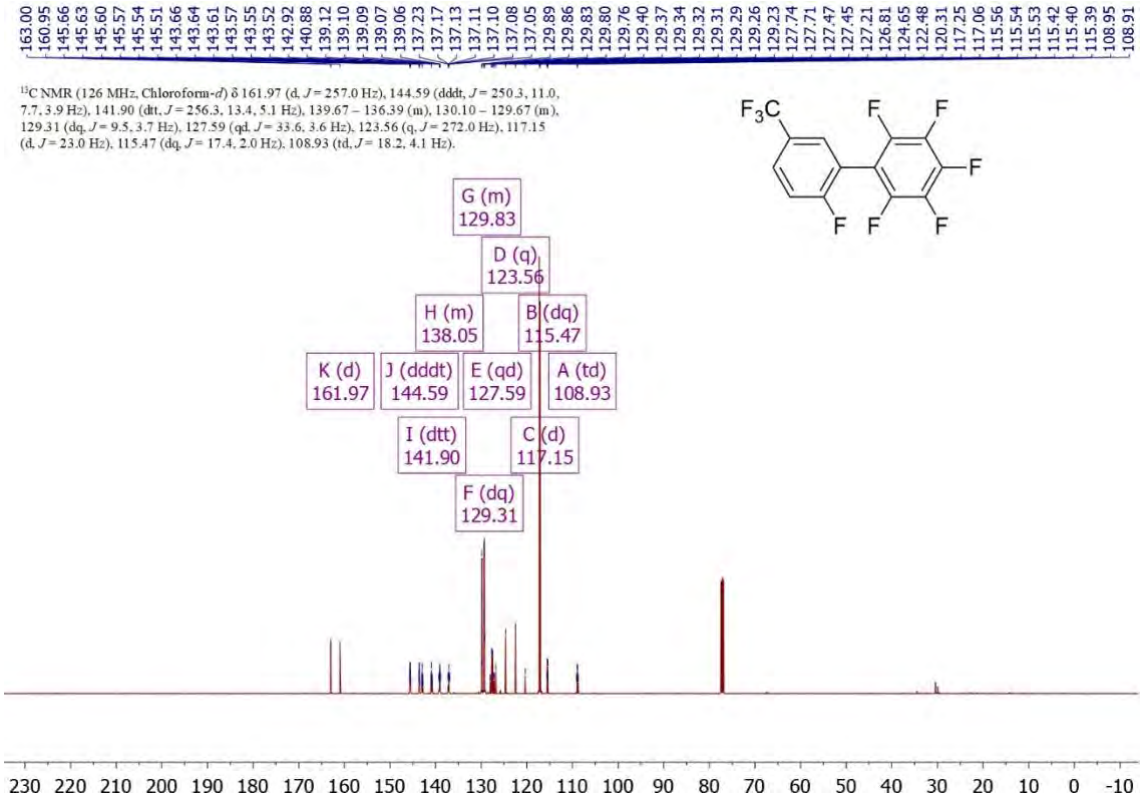


Figure ESI49. $^{13}C\{^{1}H\}$ NMR of 2,2',3,4,5,6-hexafluoro-5'-(trifluoromethyl)-1,1'-biphenyl (**3jn**) in $CDCl_3$.

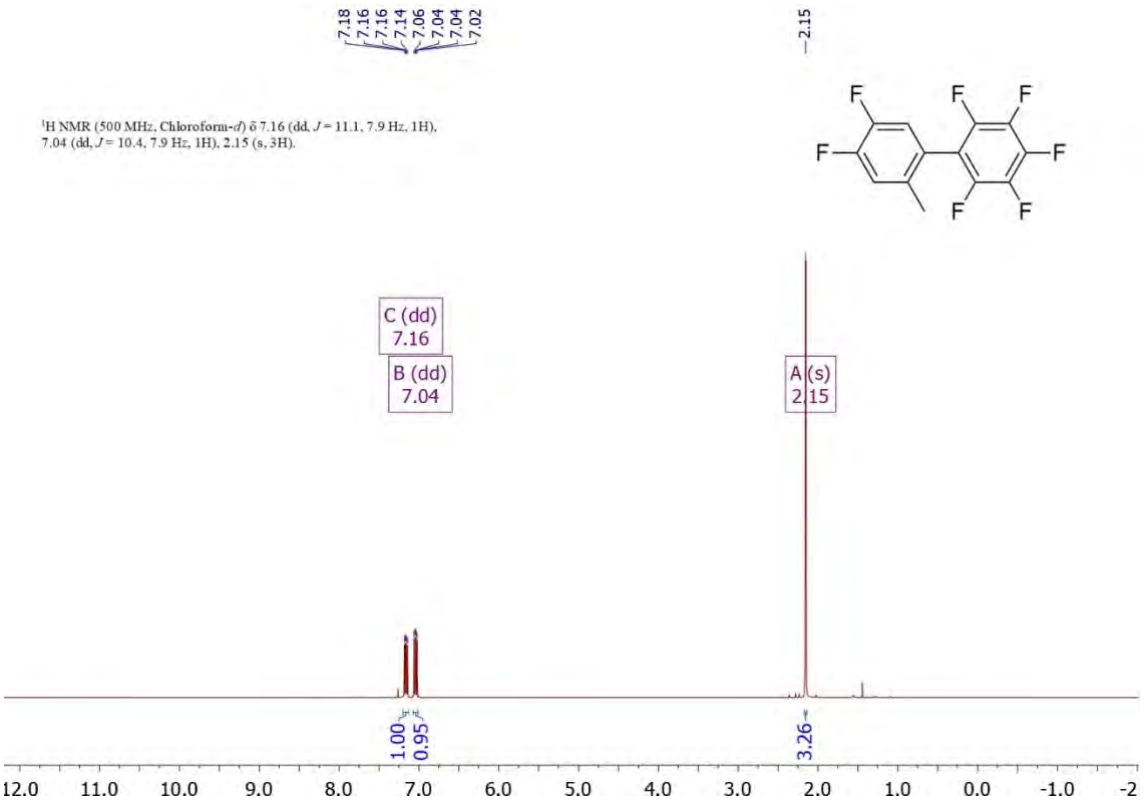


Figure ESI50. ^{1}H NMR of 2,3,4,4',5,5',6-heptafluoro-2'-methyl-1,1'-biphenyl (**3kn**) in $CDCl_3$.

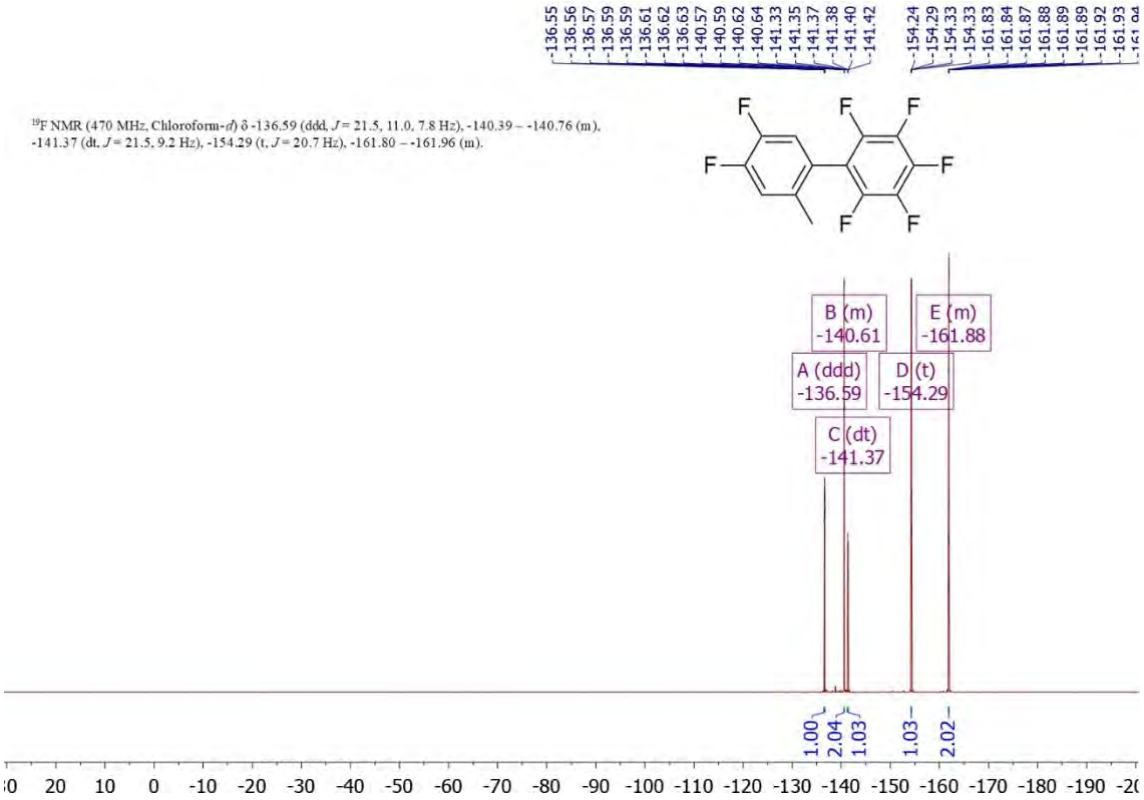


Figure ESI51. ^{19}F NMR of 2,3,4,4',5,5',6-heptafluoro-2'-methyl-1,1'-biphenyl (**3kn**) in $CDCl_3$.

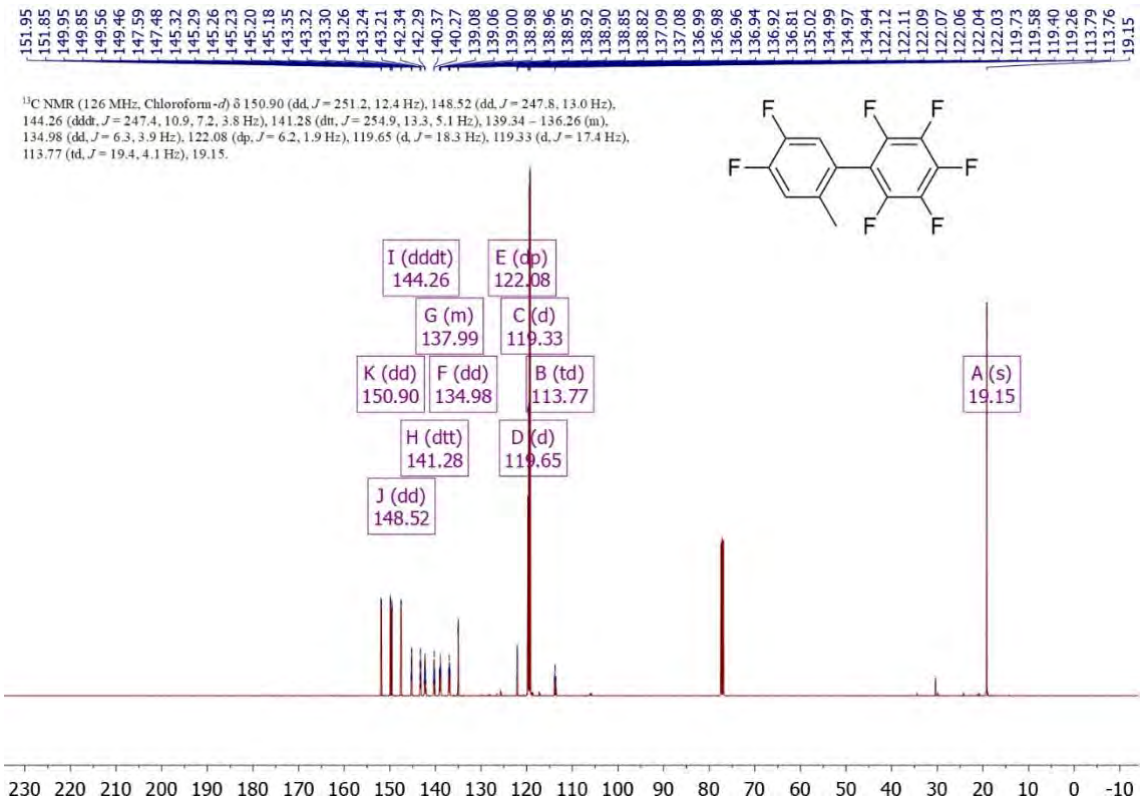


Figure ESI52. $^{13}C\{^{1}H\}$ NMR of 2,3,4,4',5,5',6-heptafluoro-2'-methyl-1,1'-biphenyl (**3kn**) in $CDCl_3$.

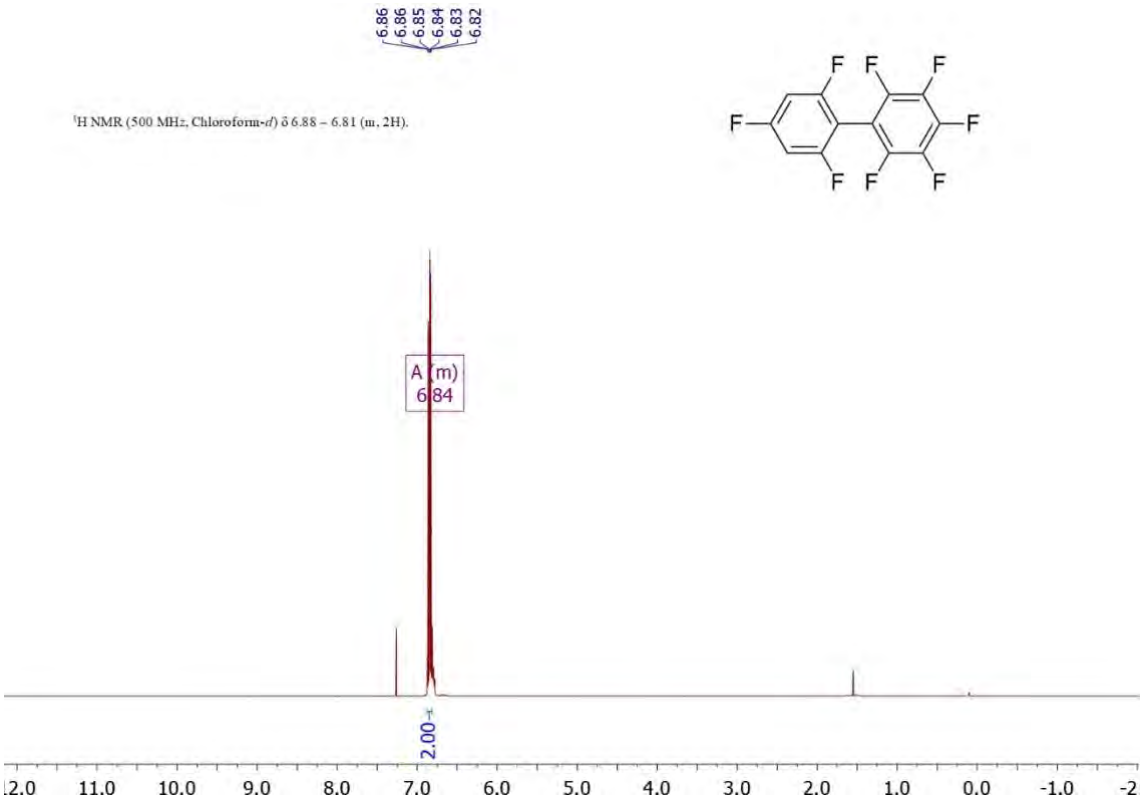


Figure ESI53. ^{1}H NMR of 2,2',3,4,4',5,6,6'-octafluoro-1,1'-biphenyl (**3ln**) in $CDCl_3$.

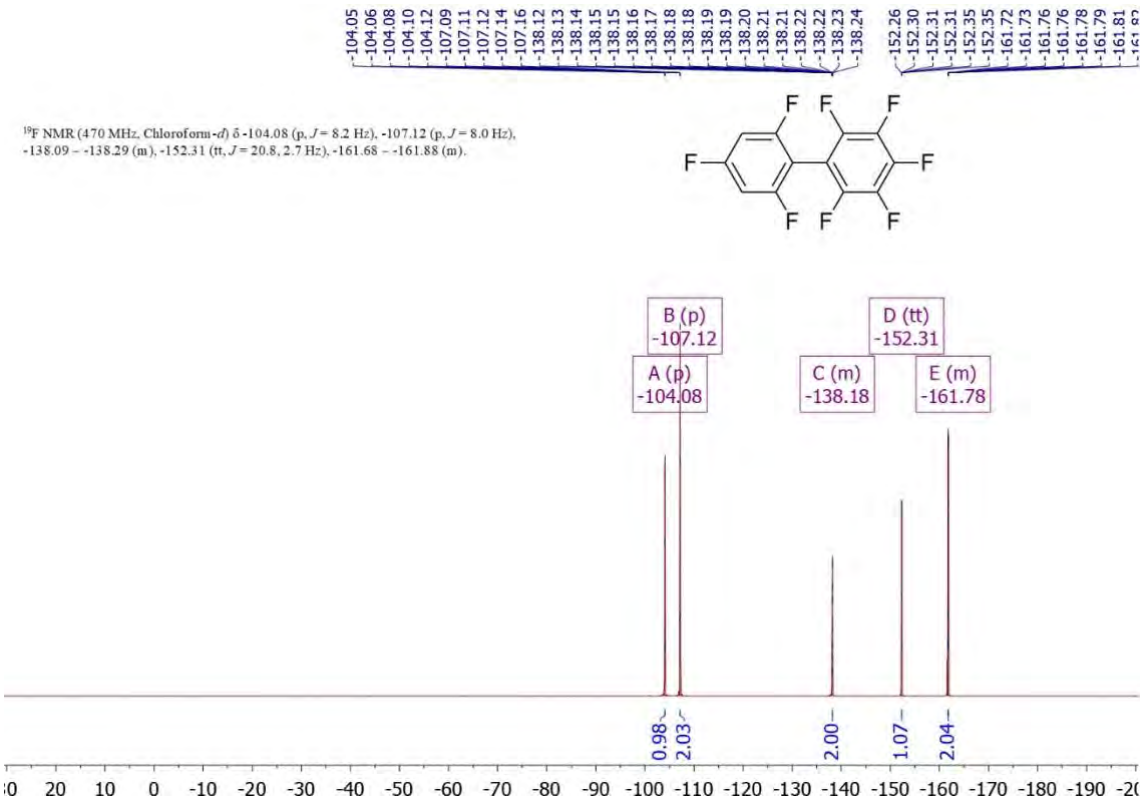


Figure ESI54. ^{19}F NMR of 2,2',3,4,4',5,6,6'-octafluoro-1,1'-biphenyl (**3ln**) in $CDCl_3$.

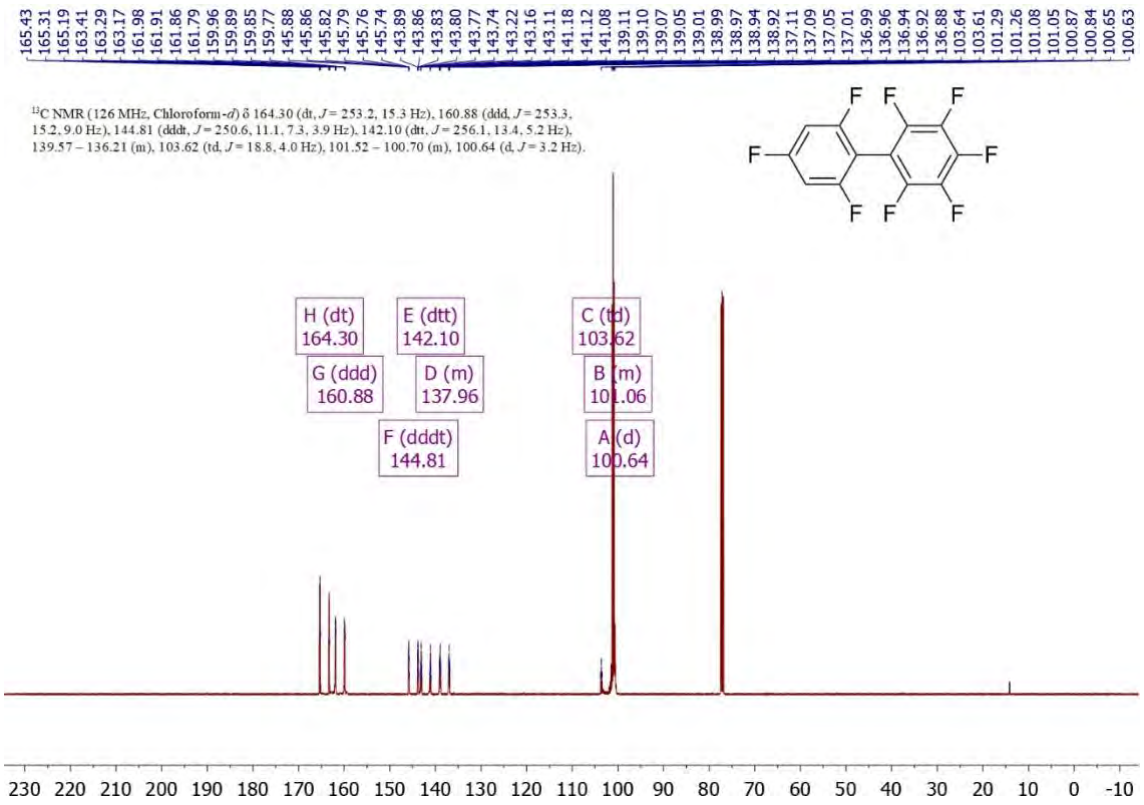


Figure ESI55. $^{13}C\{^1H\}$ NMR of 2,2',3,4,4',5,6,6'-octafluoro-1,1'-biphenyl (**3ln**) in $CDCl_3$.

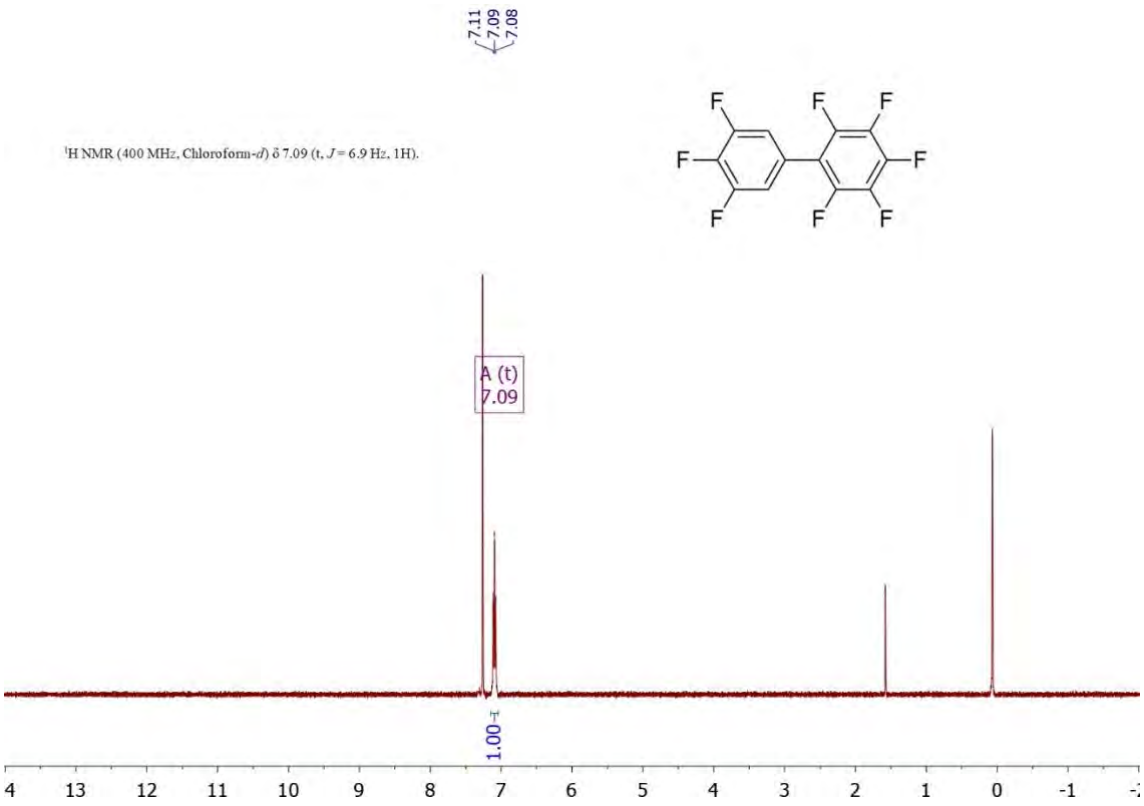


Figure ESI56. ^{1}H NMR of 2,3,3',4,4',5,5',6-octafluoro-1,1'-biphenyl (**3mn**) in $CDCl_3$.

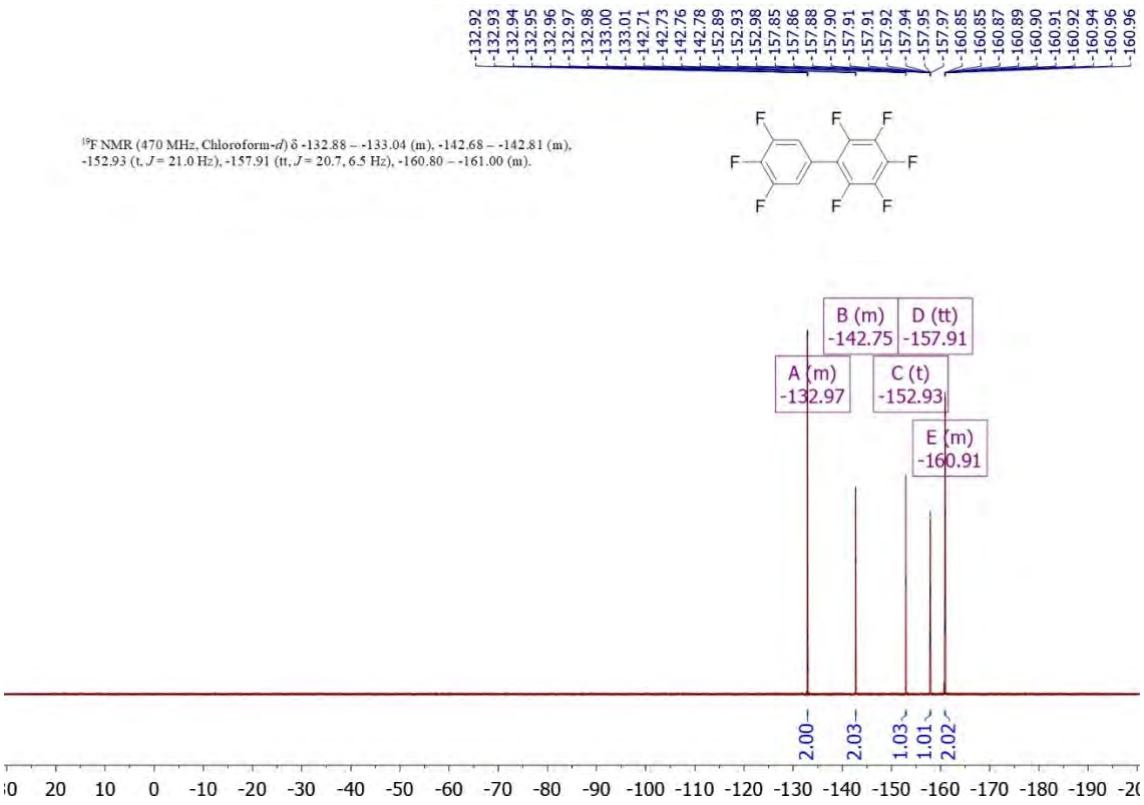


Figure ESI57. ^{19}F NMR of 2,3,3',4,4',5,5',6-octafluoro-1,1'-biphenyl (**3mn**) in $CDCl_3$.

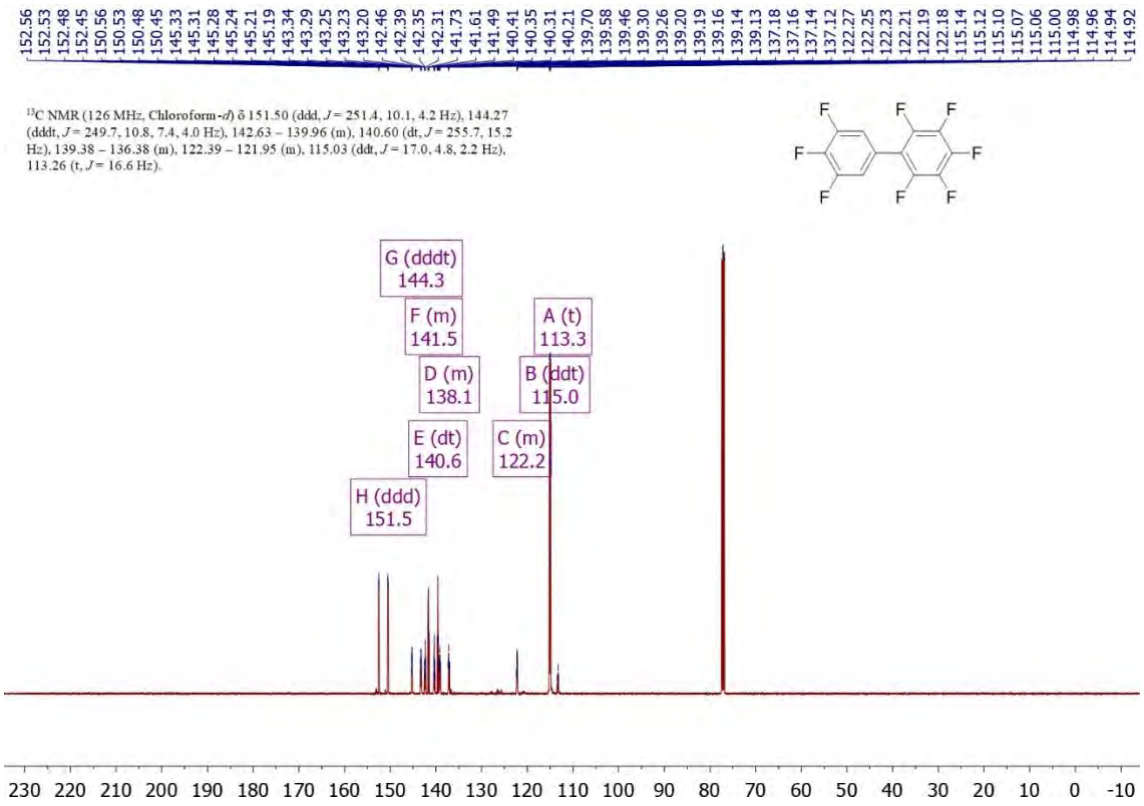


Figure ESI58. $^{13}C\{^{1}H\}$ NMR of 2,3,3',4,4',5,5',6-octafluoro-1,1'-biphenyl (**3mn**) in $CDCl_3$.

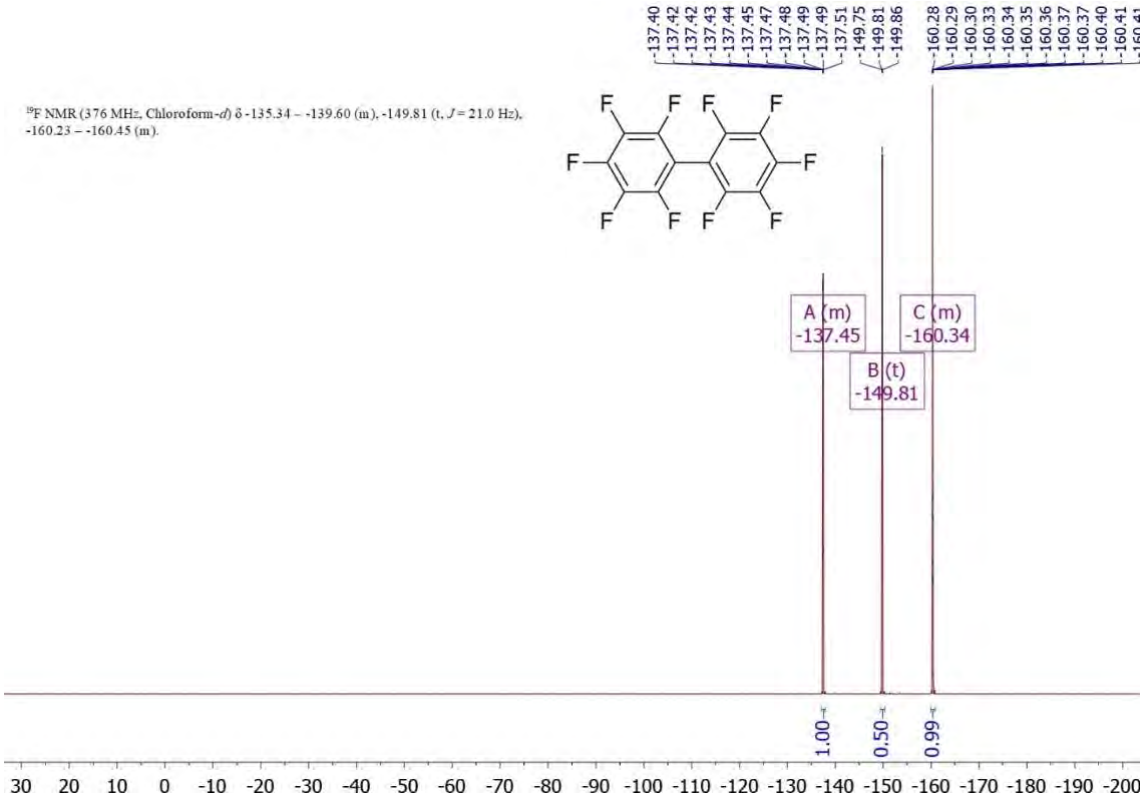


Figure ESI59. ^{19}F NMR of perfluoro-1,1'-biphenyl (**3nn**) in $CDCl_3$.

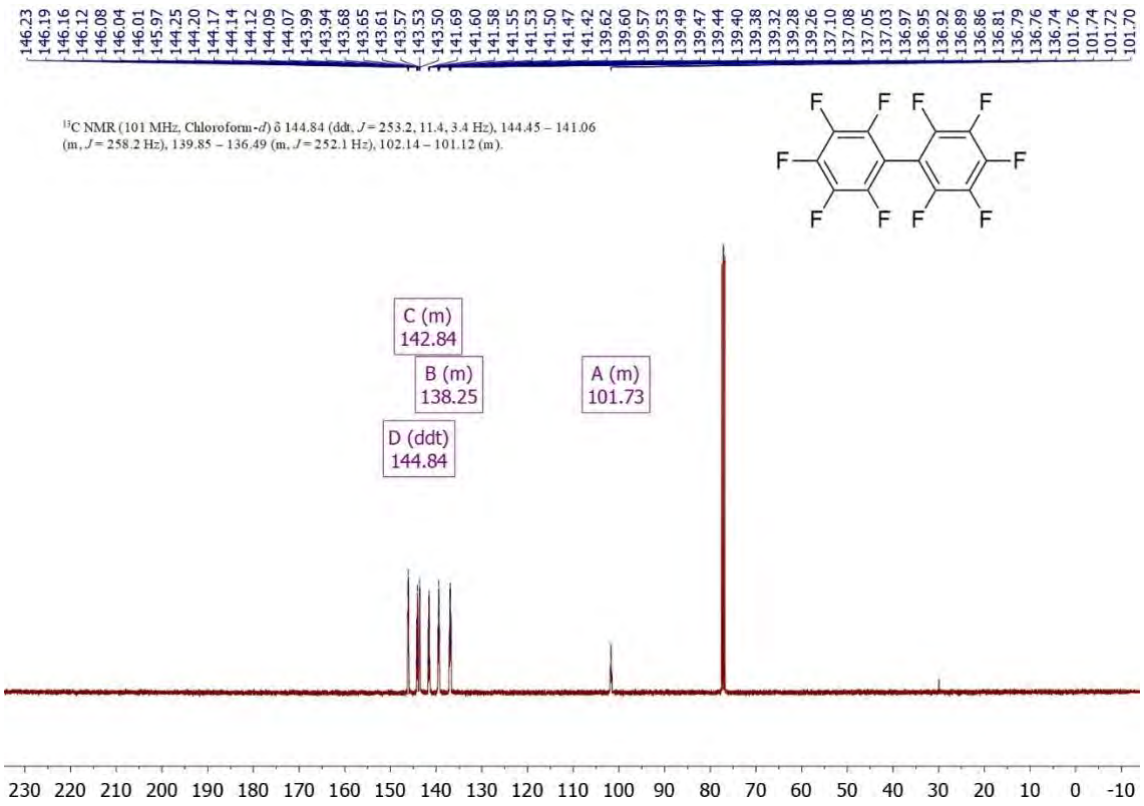


Figure ESI60. $^{13}C\{^{1}H\}$ NMR of perfluoro-1,1'-biphenyl (**3nn**) in $CDCl_3$.

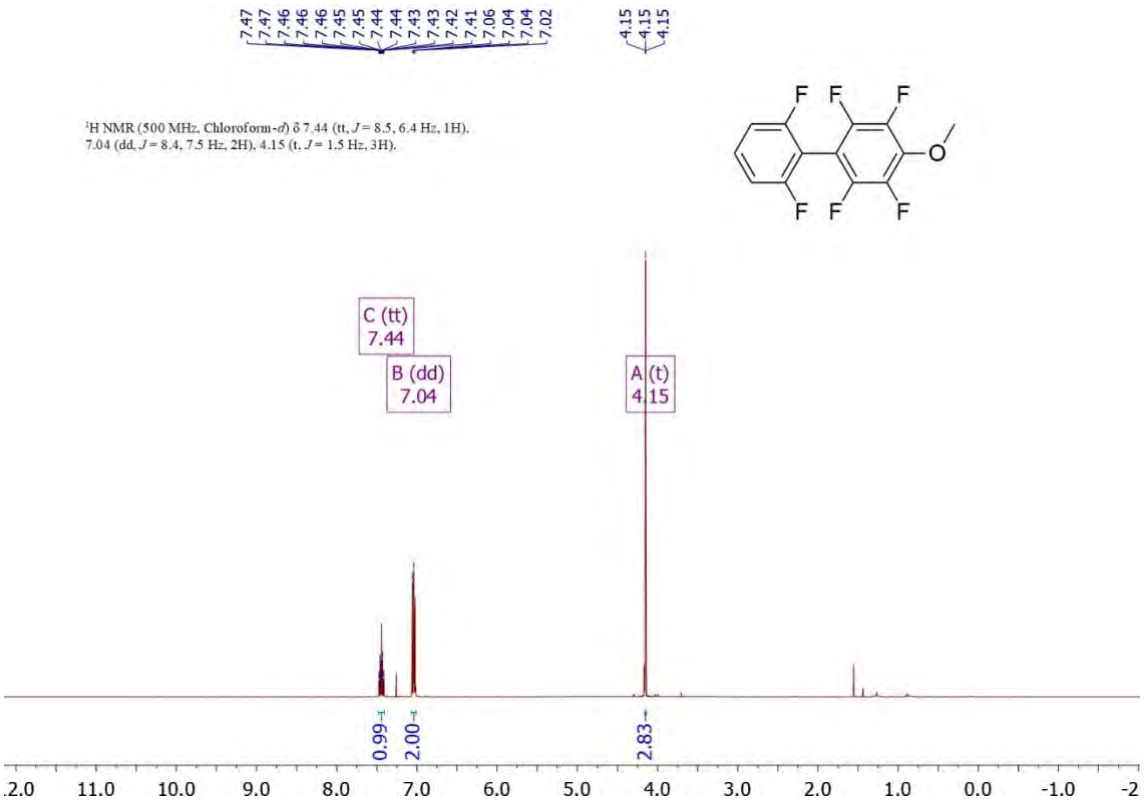


Figure ESI61. ^{1}H NMR of 2,2',3,5,6,6'-hexafluoro-4-methoxy-1,1'-biphenyl (**3ap**) in $CDCl_3$.

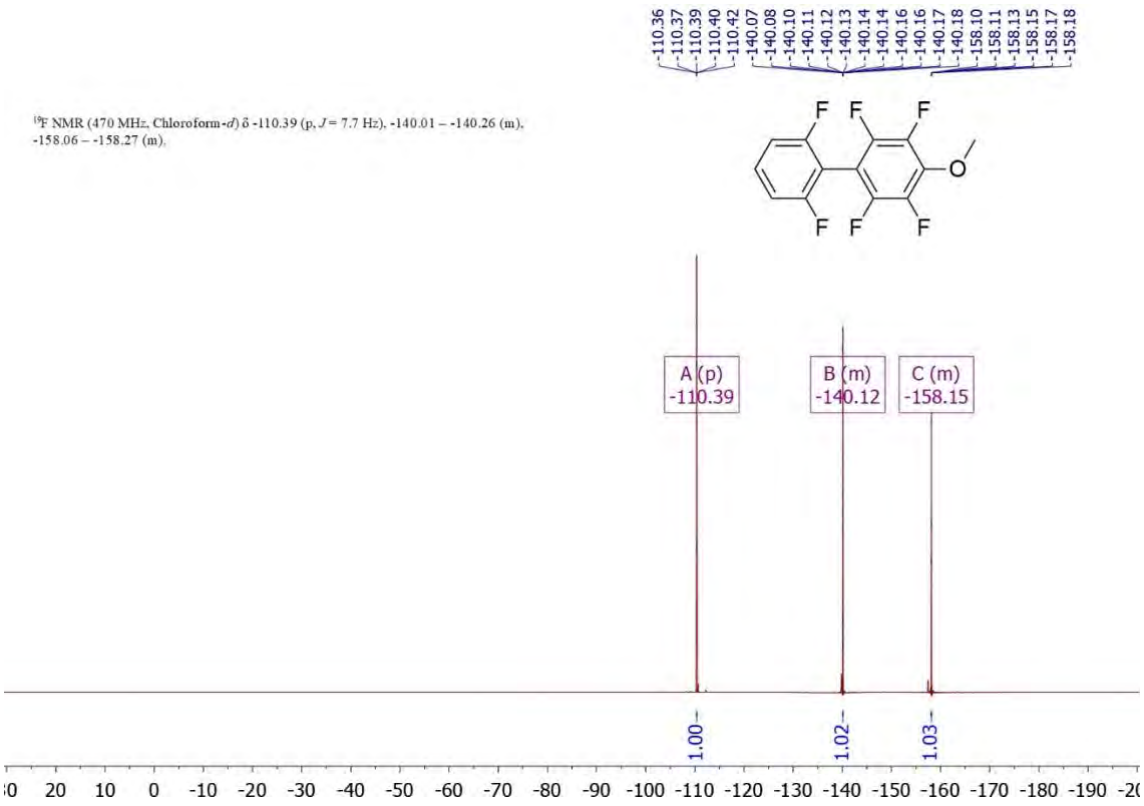


Figure ESI62. ^{19}F NMR of 2,2',3,5,6,6'-hexafluoro-4-methoxy-1,1'-biphenyl (**3ap**) in $CDCl_3$.

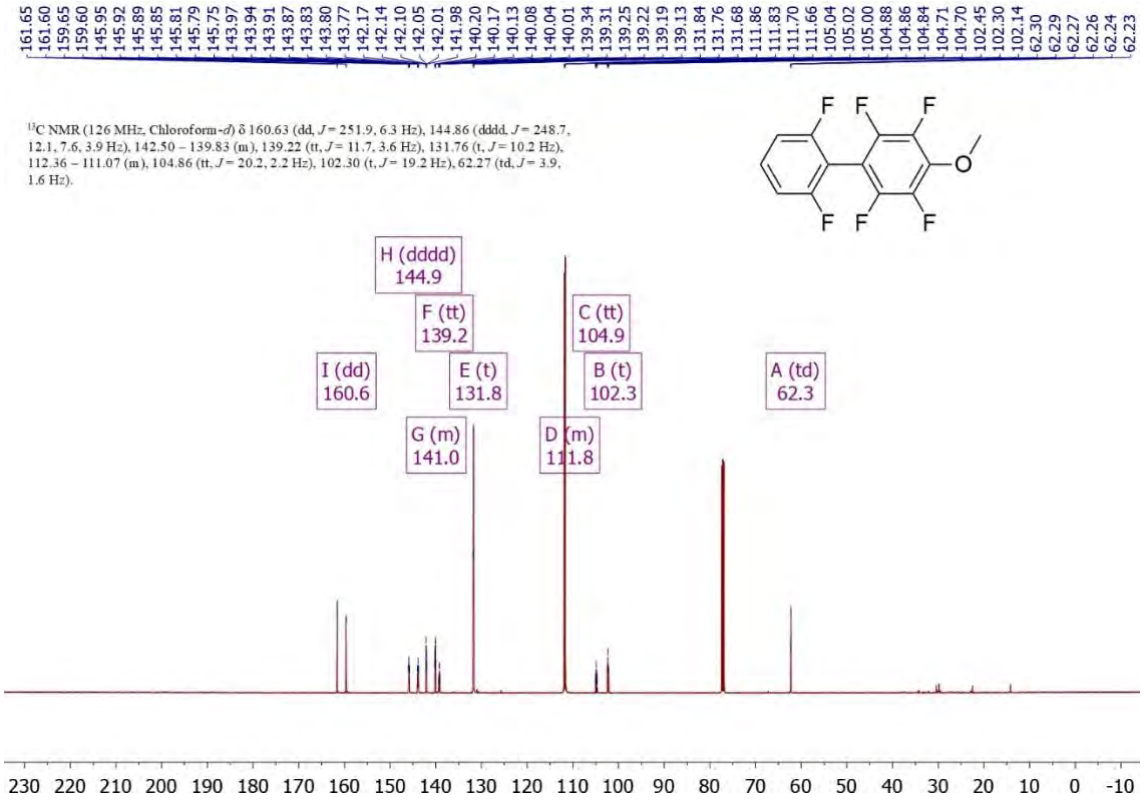


Figure ESI63. $^{13}C\{^1H\}$ NMR of 2,2',3,5,6,6'-hexafluoro-4-methoxy-1,1'-biphenyl (**3ap**) in $CDCl_3$.

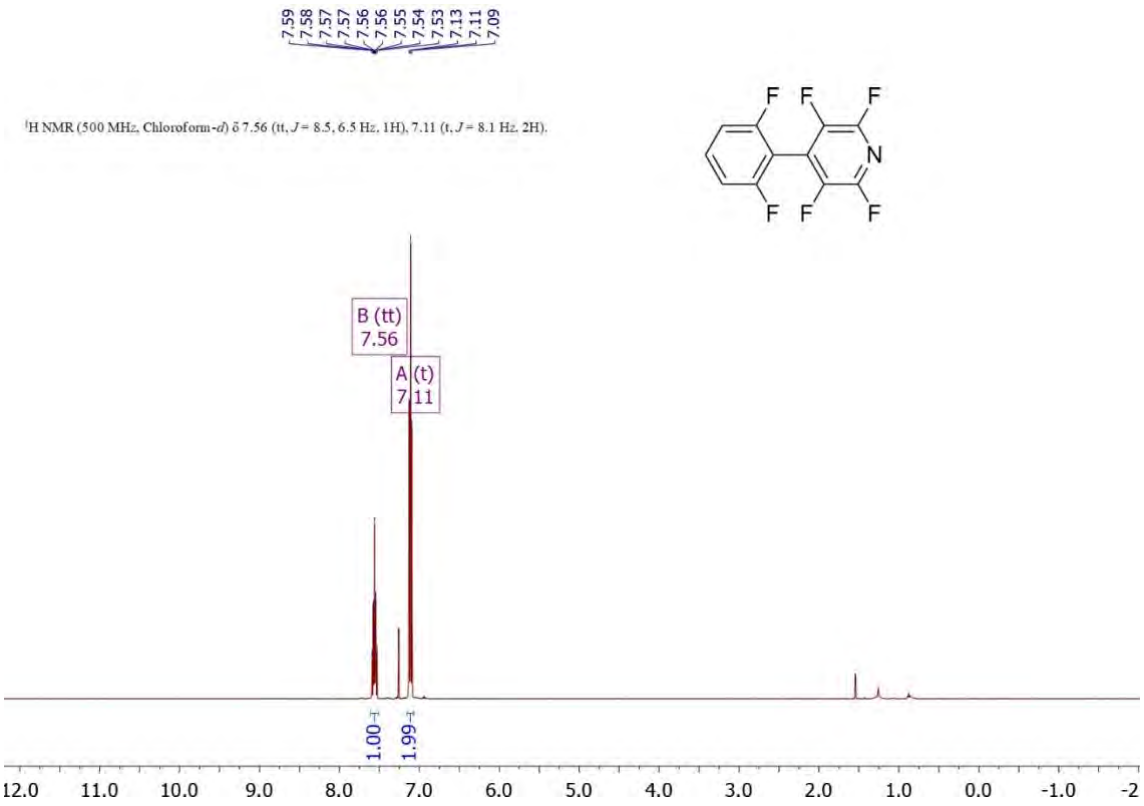


Figure ESI64. ^{1}H NMR of 4-(2,6-difluorophenyl)-2,3,5,6-tetrafluoropyridine (**3aq**) in $CDCl_3$.

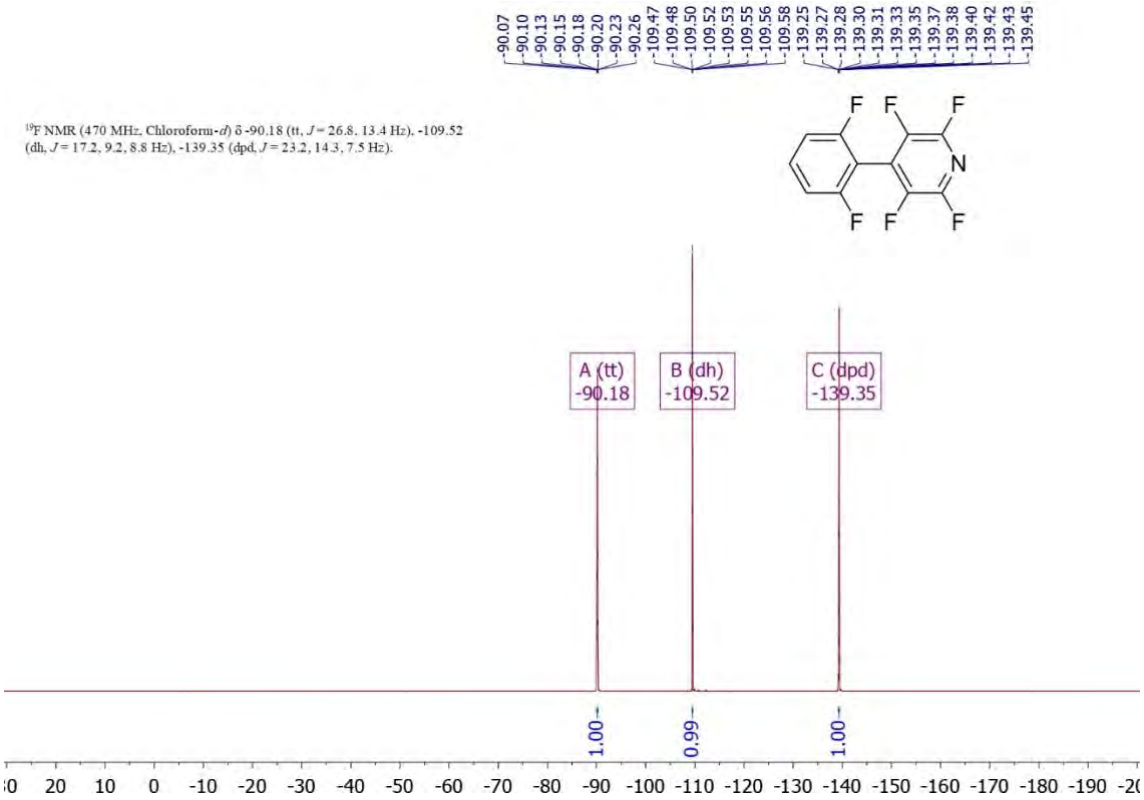


Figure ESI65. ^{19}F NMR of 4-(2,6-difluorophenyl)-2,3,5,6-tetrafluoropyridine (**3aq**) in $CDCl_3$.

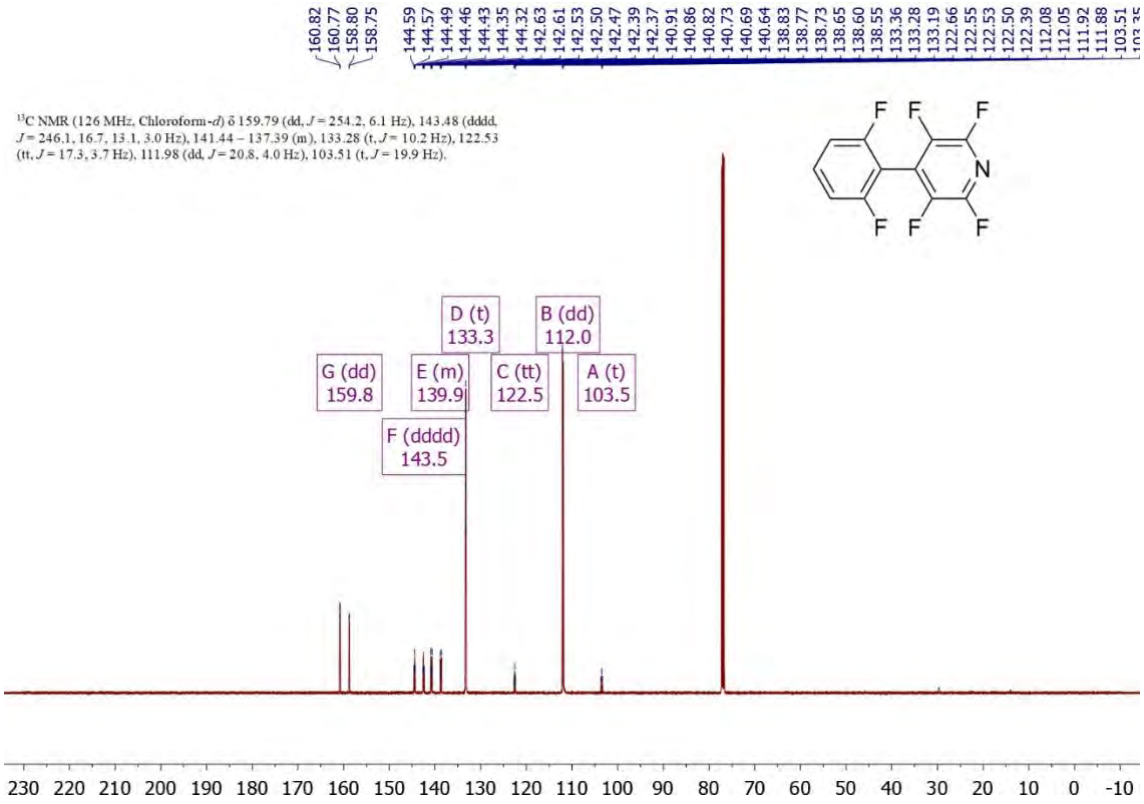


Figure ESI66. $^{13}C\{^{1}H\}$ NMR of 4-(2,6-difluorophenyl)-2,3,5,6-tetrafluoropyridine (**3aq**) in $CDCl_3$.

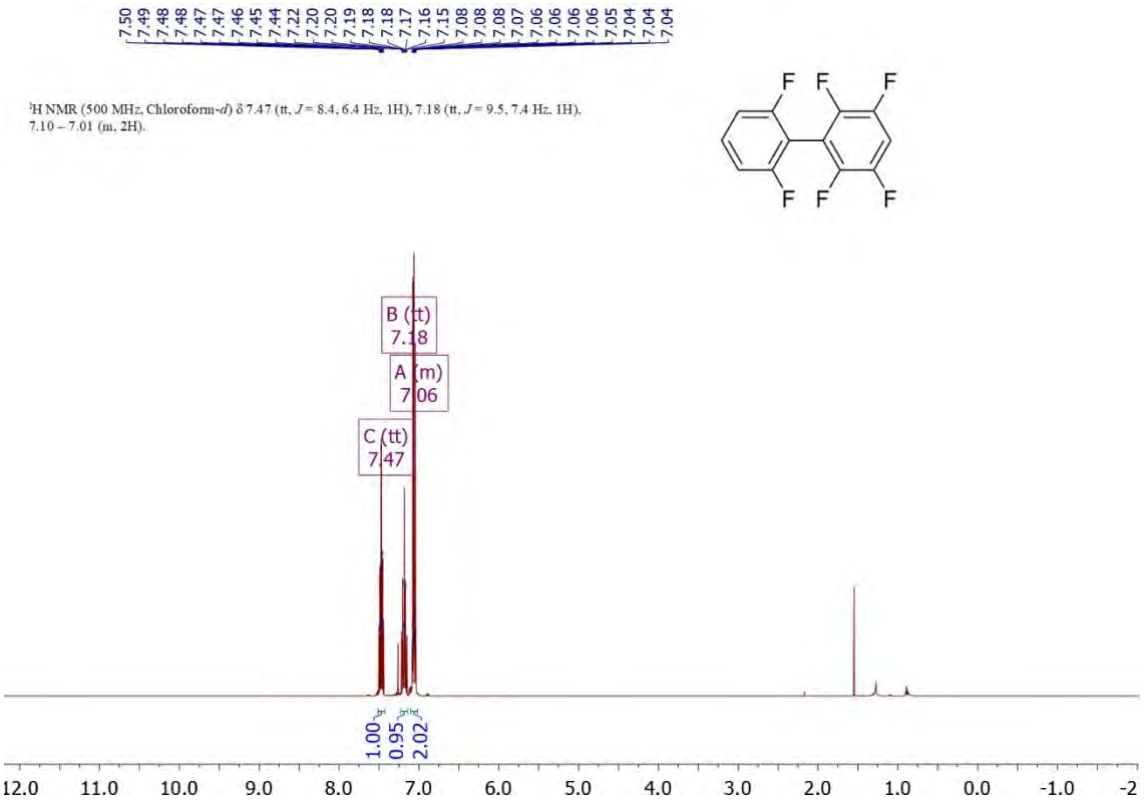


Figure ESI67. ^{1}H NMR of 2,2',3,5,6,6'-hexafluoro-1,1'-biphenyl (**3as**) in $CDCl_3$.

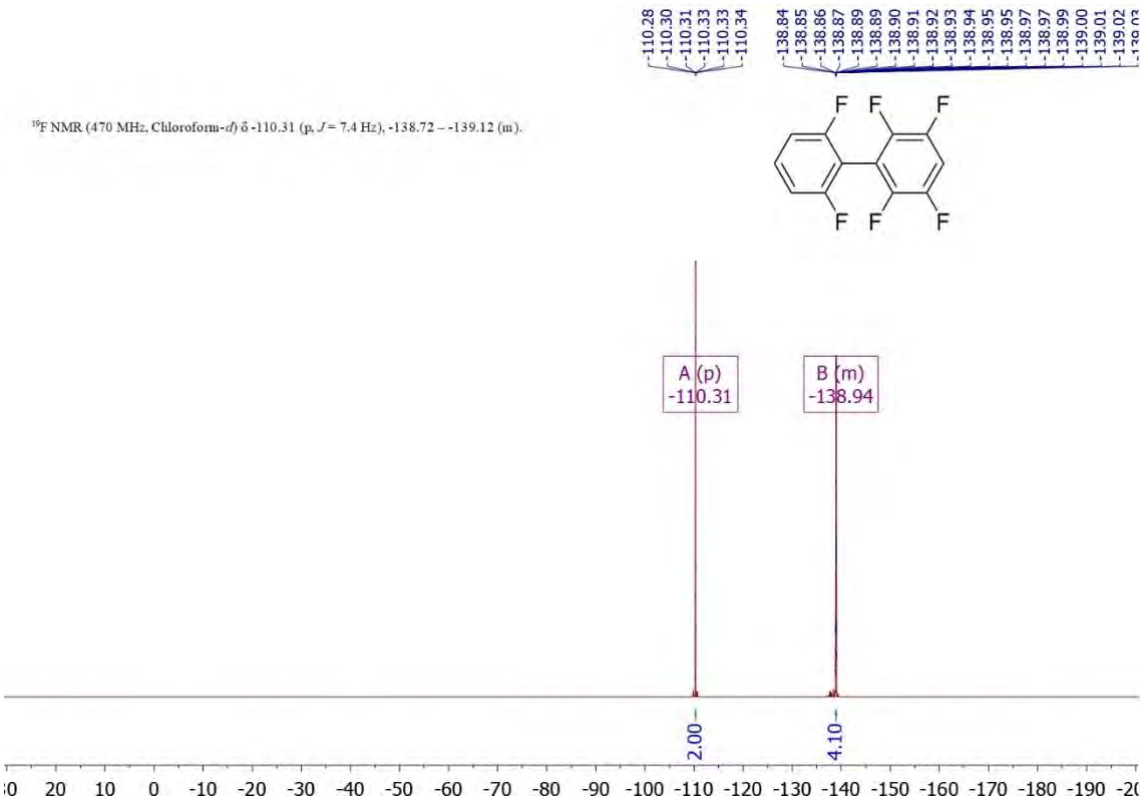


Figure ESI68. ^{19}F NMR of 2,2',3,5,6,6'-hexafluoro-1,1'-biphenyl (**3as**) in $CDCl_3$.

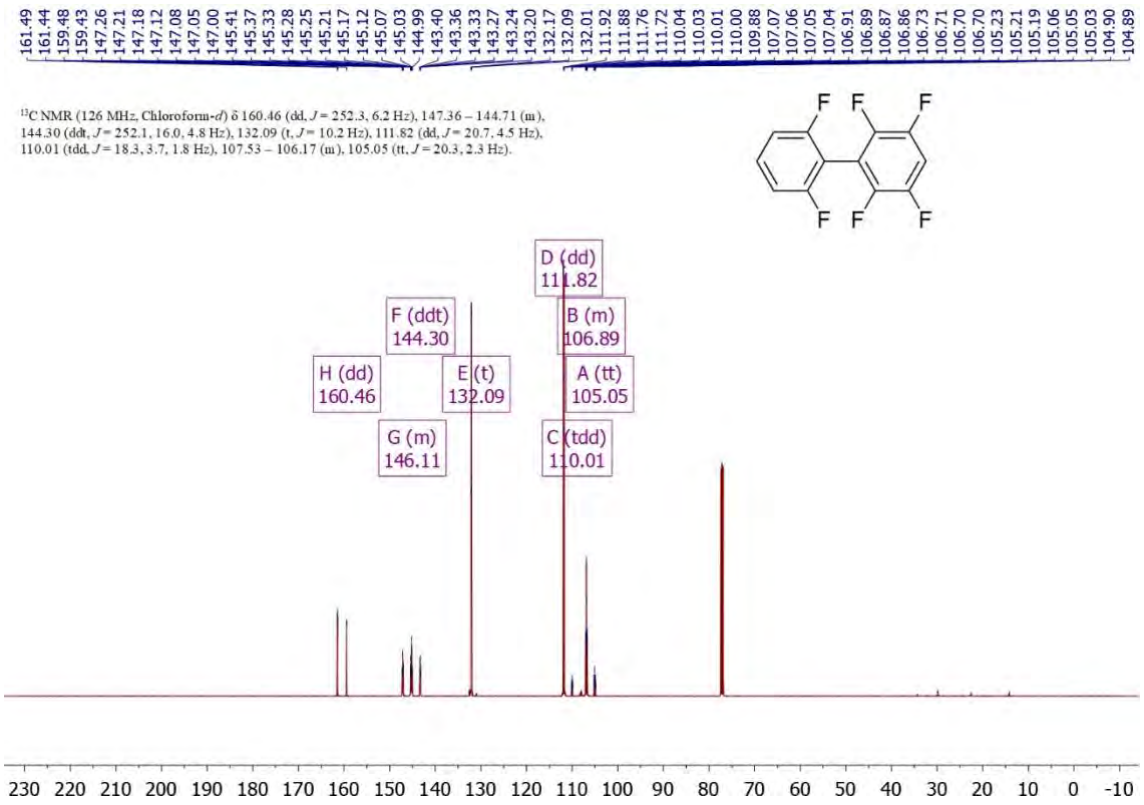


Figure ESI69. $^{13}C\{^1H\}$ NMR of 2,2',3,5,6,6'-hexafluoro-1,1'-biphenyl (**3as**) in $CDCl_3$.

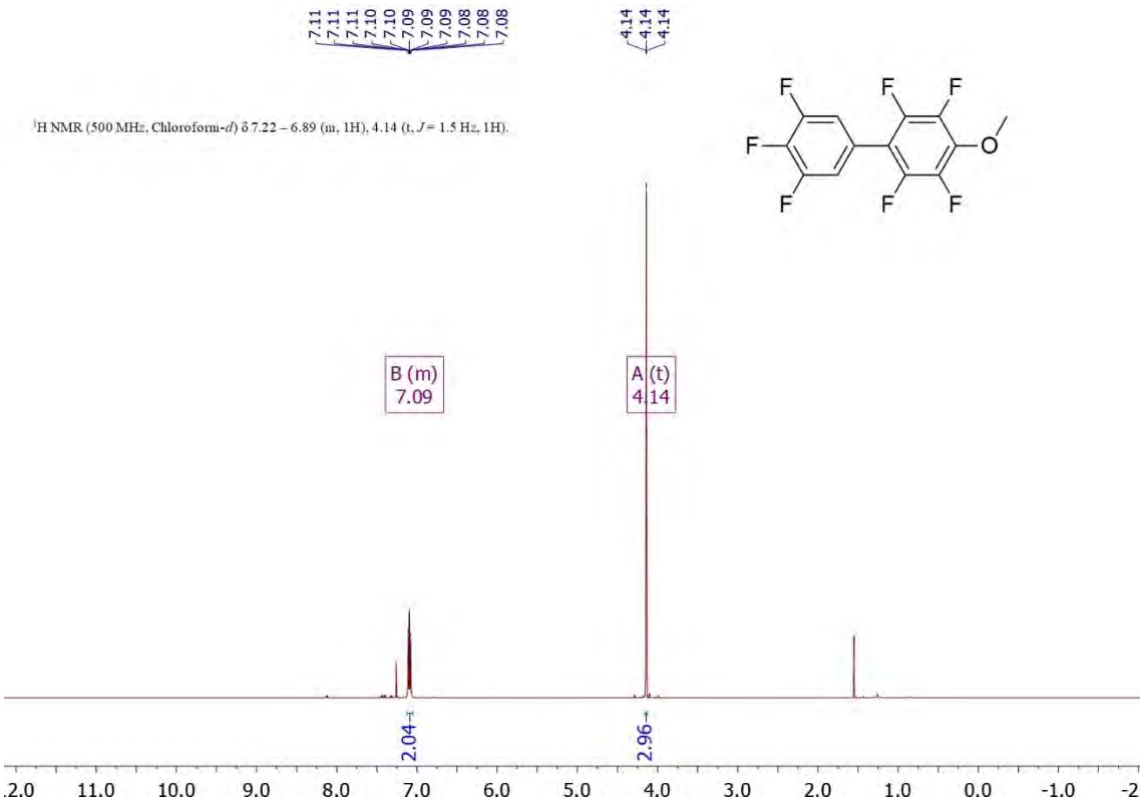


Figure ESI70. ^{1}H NMR of 2,3,3',4',5,5',6-heptafluoro-4-methoxy-1,1'-biphenyl (**3mp**) in $CDCl_3$.

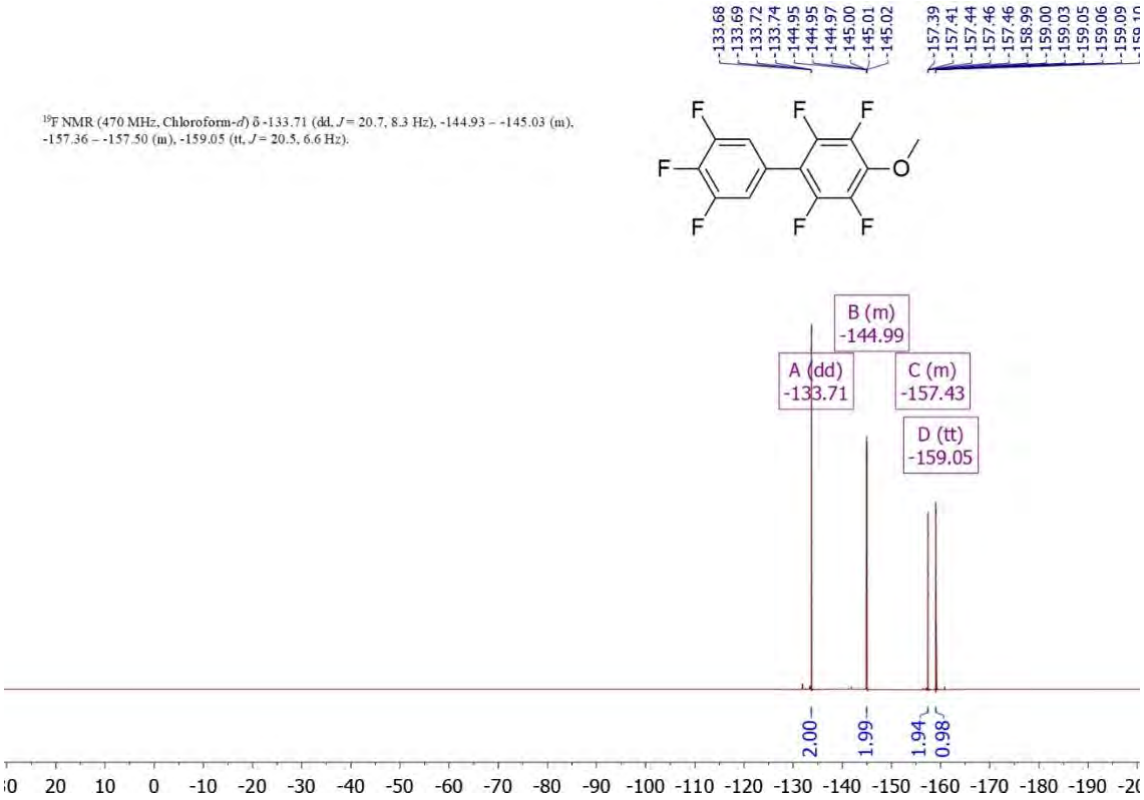


Figure ESI71. ^{19}F NMR of 2,3,3',4',5,5',6-heptafluoro-4-methoxy-1,1'-biphenyl (**3mp**) in $CDCl_3$.

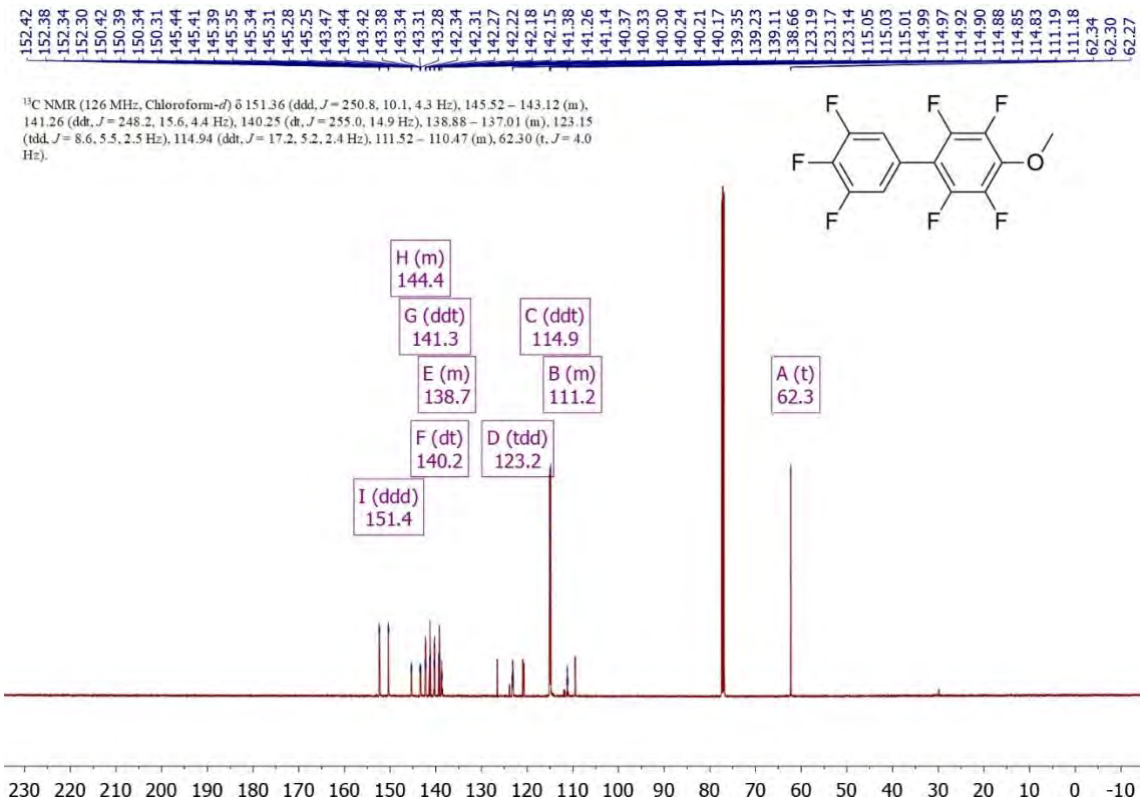


Figure ESI72. $^{13}C\{^{1}H\}$ NMR of 2,3,3',4',5,5',6-heptafluoro-4-methoxy-1,1'-biphenyl (**3mp**) in $CDCl_3$.

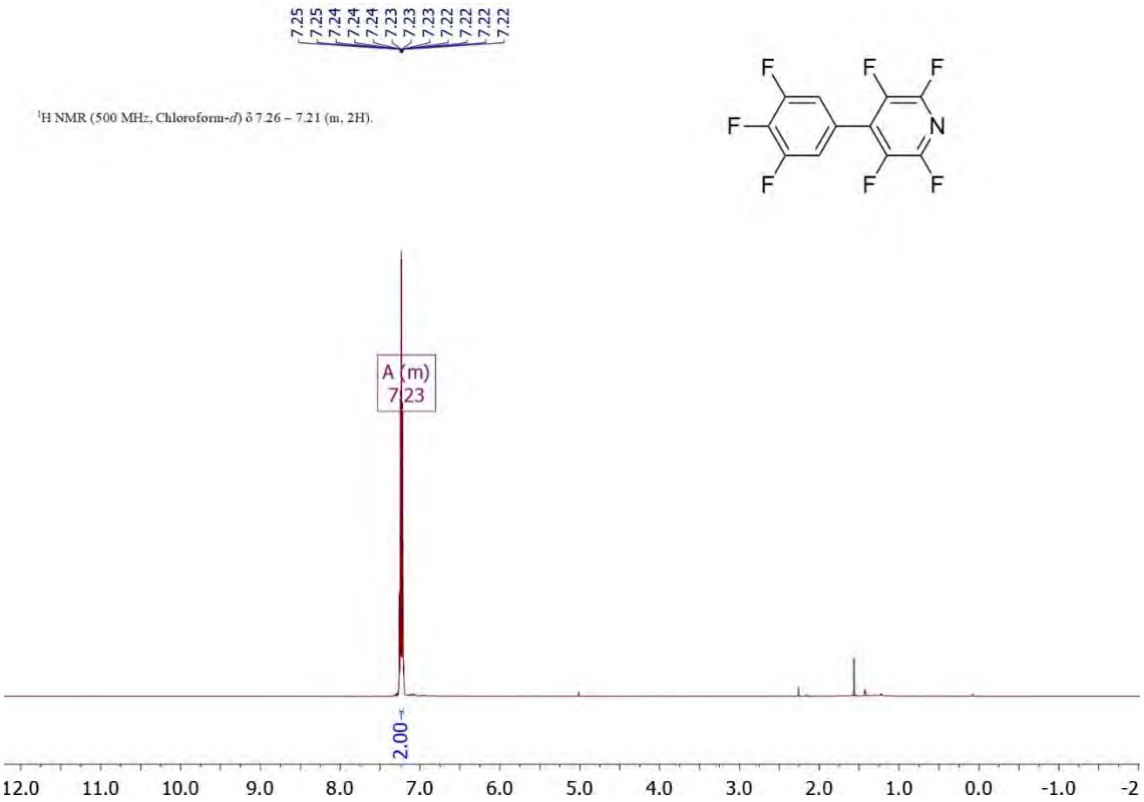


Figure ESI73. ^{1}H NMR of 2,3,5,6-tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine (**3mq**) in $CDCl_3$.

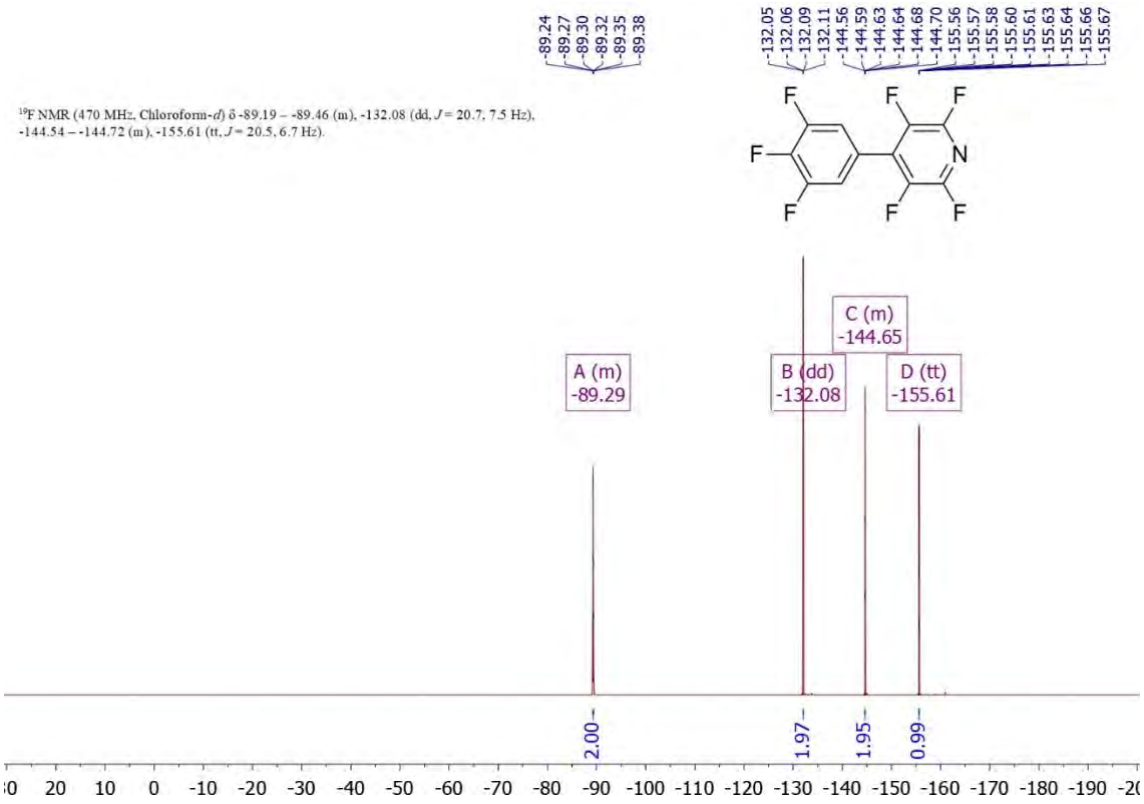


Figure ESI74. ^{19}F NMR of 2,3,5,6-tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine (**3mq**) in $CDCl_3$.

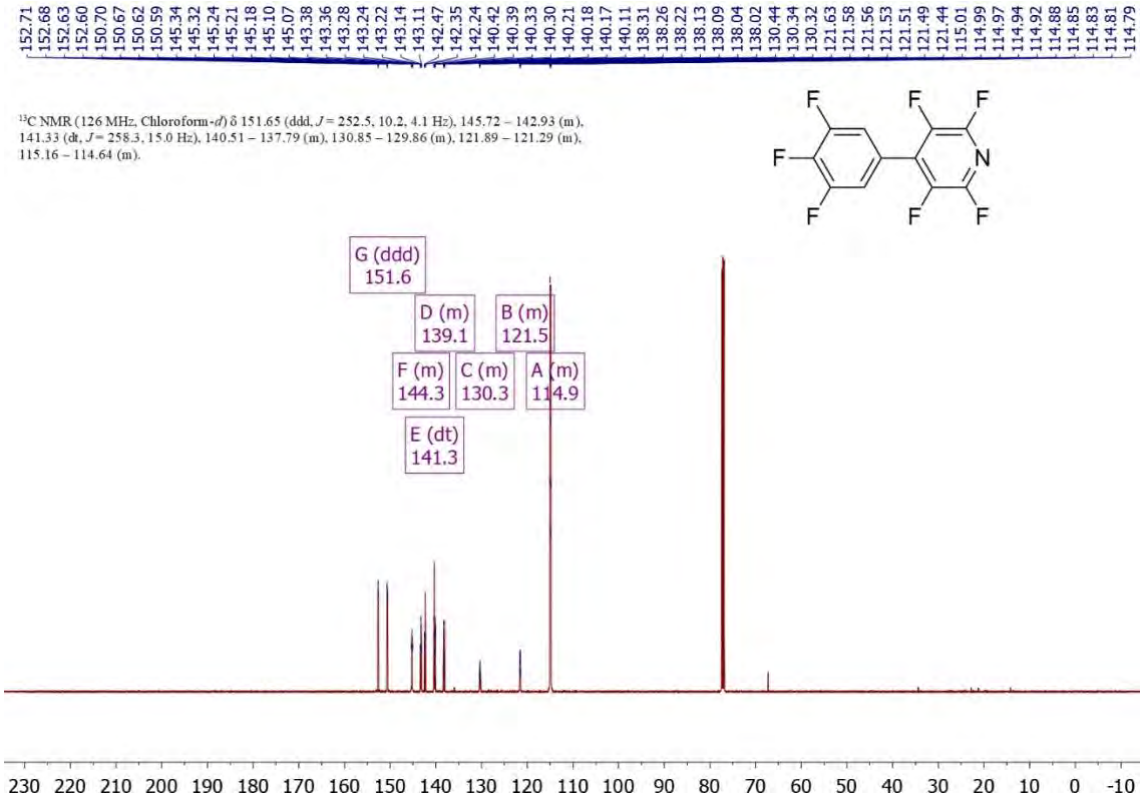


Figure ESI75. $^{13}C\{^1H\}$ NMR of 2,3,5,6-tetrafluoro-4-(3,4,5-trifluorophenyl)pyridine (**3mq**) in $CDCl_3$.

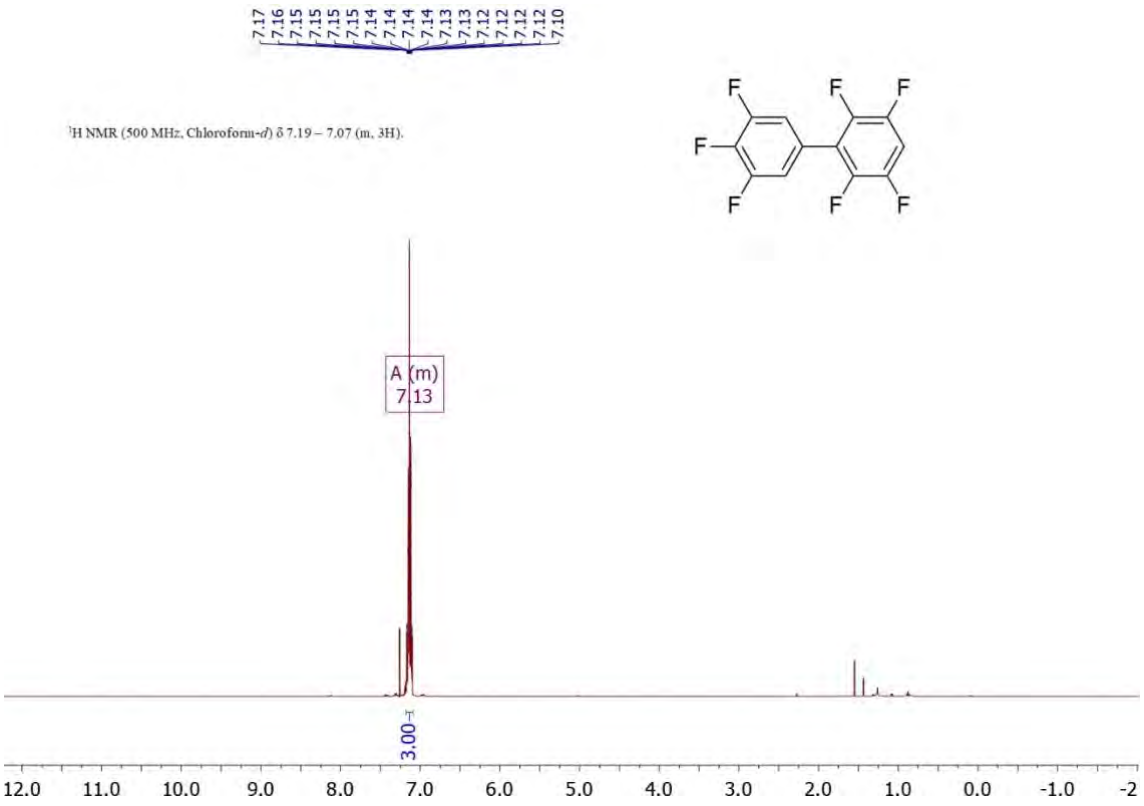


Figure ESI76. ^{1}H NMR of 2,3,3',4',5,5',6-heptafluoro-1,1'-biphenyl (**3ms**) in $CDCl_3$.

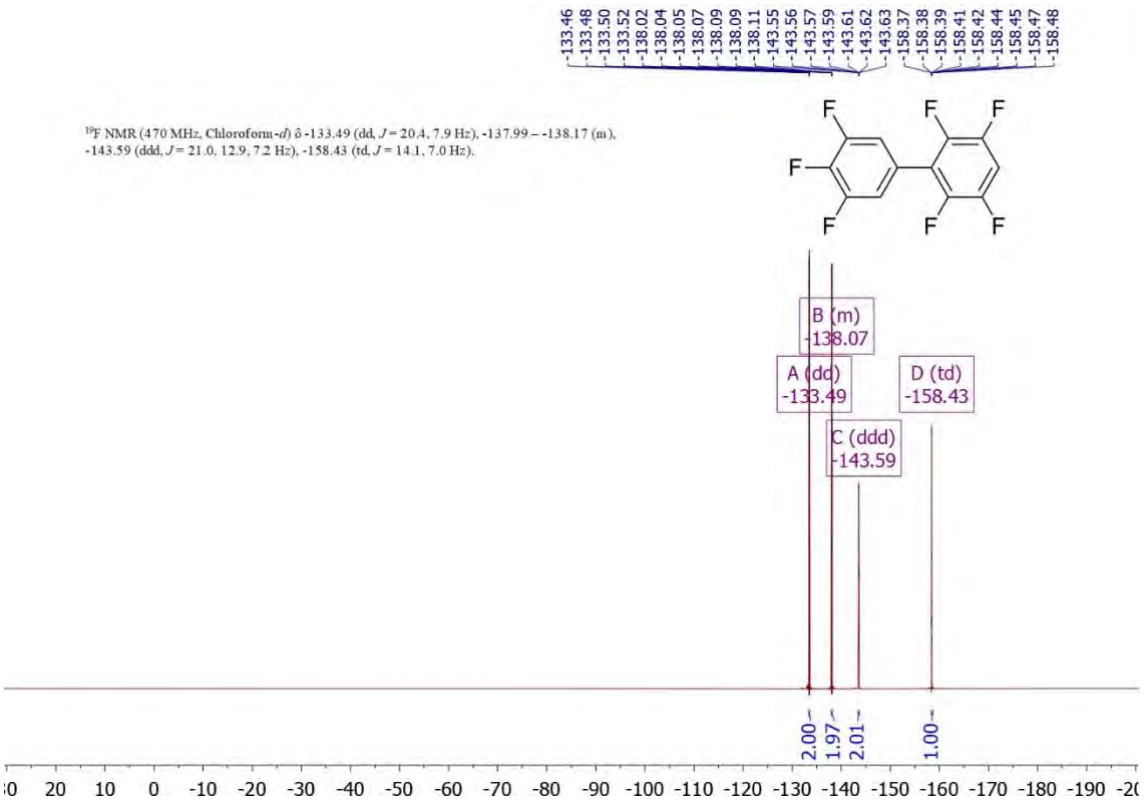


Figure ESI77. ^{19}F NMR of 2,3,3',4',5,5',6-heptafluoro-1,1'-biphenyl (**3ms**) in $CDCl_3$.

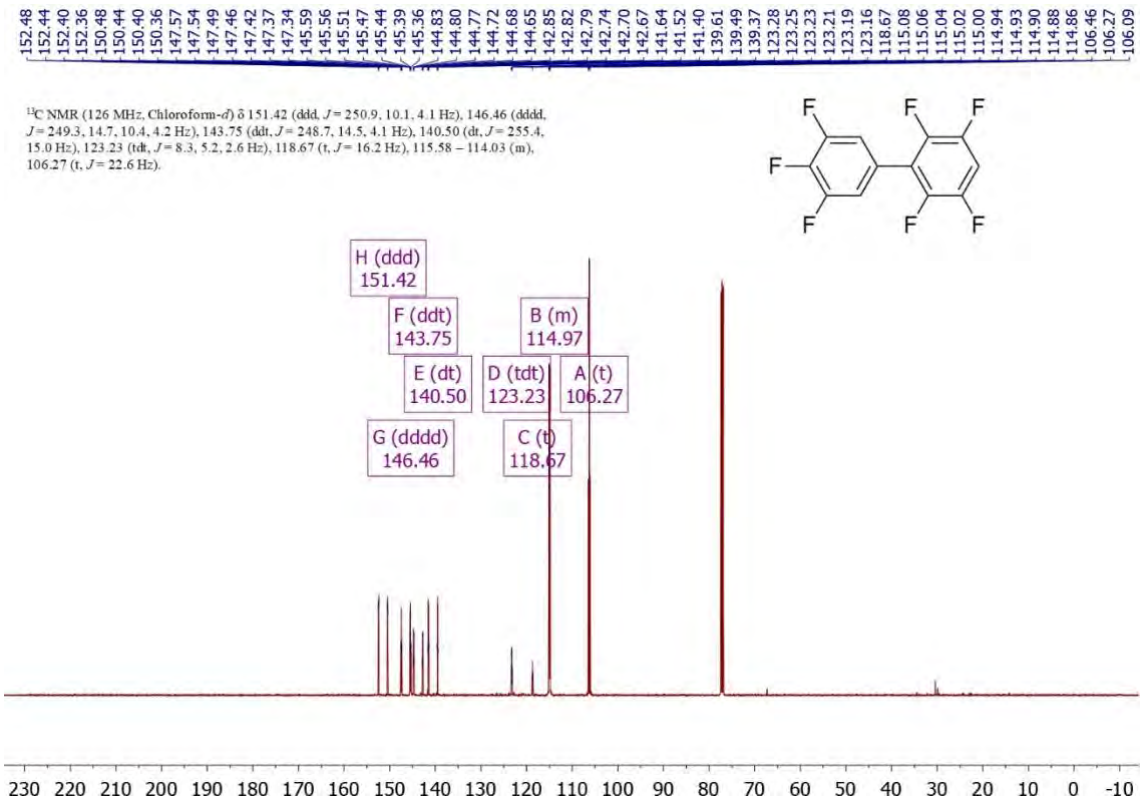


Figure ESI78. $^{13}C\{^{1}H\}$ NMR of 2,3,3',4',5,5',6-heptafluoro-1,1'-biphenyl (**3ms**) in $CDCl_3$.

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